

**High-throughput multifunctional materials characterization with
real-time analytics and feedback**

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Abstract

Novel functional materials are enabling transformational breakthroughs in energy, electronics, manufacturing and medicine. Development of new materials is being fueled by advances in high-performance computing, robotics, and high-throughput methods for materials synthesis and processing. To close the feedback loop between materials design, synthesis and functionality, novel materials must be rapidly screened for stability and functionality under a broad range of ambient environmental conditions. We developed an automated system for simultaneous probing of electrical, optical, gravimetric, and viscoelastic properties of materials under controlled environments, enabling characterization of material response to temperature, pressure, humidity, light intensity, and ambient gas/vapor composition. Control of environmental conditions, experimental procedures, and data acquisition were performed using custom integrated software with on-the-fly data processing and analytics. Real-time material response was used as feedback for iterative optimization of experiment settings, allowing automated initiation and termination of experimental procedures and reduced need for human researcher input. The system was used to characterize environmental response and sensing performance of a broad range of materials including polymers, metal oxides, organic small molecules, biomolecules, perovskites, nanotubes and two-dimensional materials. We found that material response to environment was generally mediated by charge transfer with adsorbate molecules, mechano-structural changes caused by diffusion of adsorbates into adsorbent films, production of mobile ions due to salt dissociation and formation of surface water layers, and photoexcitation of adsorbents by UV radiation. Material response often exhibited mixed-kinetics consisting of rapid gravimetric response during sorption of adsorbates on active surface sites, and slow electrical response resulting from diffusion of adsorbates into the bulk films.

Here, we describe details of the multifunctional characterization system, show examples of functional materials characterized by the system, and describe potential future improvements to the system. Future opportunities for development include (i) integration of combinatorial synthesis methods to close the feedback loop between synthesis and characterization, (ii) integration of computational modeling for real-time feedback between experiment and simulation, (iii) database integration for creation of a materials expert system, and (iv) in situ diagnostics on X-ray and/or neutron beamlines for probing structure-function relationships under dynamic environments.

Table of Contents

Chapter 1: Introduction	1
Background and motivation	2
Current challenges	5
Chapter 2: Experimental methods and workflow	9
Quartz crystal microbalance	10
Integrated multifunctional environmental chamber	14
Integrated control and analysis software	17
Personal contributions	24
Chapter 3: Oxygen and humidity response of CuPc	25
Abstract	26
Introduction	27
Experiment	29
Results and discussion	30
Conclusions	40
Chapter 4: Humidity response of water-soluble CuPc	42
Abstract	43
Introduction	44
Experiment	46
Results and discussion	47
Film morphology	47
Gravimetric humidity response	49
Modeling of adsorption kinetics	53
Optical response to humidity	56
Electrical response to humidity	58
Multimodal humidity detection sensitivity	62
Conclusions	65
Chapter 5: Oxygen, humidity, UV light response of CNTs	67

Abstract	68
Introduction	69
Experiment	74
Results and discussion.....	75
Conclusions.....	85
Chapter 6: Humidity response of PEDOT:PSS	86
Abstract	87
Introduction	88
Experiment	90
Results and discussion.....	91
Nanoscale response to humidity.....	91
AC electrical response to humidity.....	96
Optical response to humidity.....	99
Conclusions.....	104
Chapter 7: Humidity response of ZnO-infiltrated SU-8.....	105
Abstract	106
Introduction	107
Experiment	110
Results and discussion.....	113
Microstructure and chemical depth profiling.....	113
Gravimetric gas-sensing properties	116
Origins of UV-activated gas sensing.....	119
Investigation of O ₂ and H ₂ O adsorption	122
Performance of gravimetric vapor sensing	125
Optical and electrical properties.....	129
Conclusions.....	132
Chapter 8: Humidity response of H-intercalated MXene	133
Abstract	134
Introduction	135
Experiment	136

Results and discussion.....	138
DC resistive and gravimetric sensing.....	138
Frequency-dependent electrical sensing	140
Low-power current sensing.....	143
Mechanism of gravimetric response to water vapor.....	143
Conclusions.....	149
Chapter 9: Humidity response of ion-intercalated MXenes	150
Abstract	152
Introduction	152
Experiment	154
Results and discussion.....	156
Conclusions.....	163
Chapter 10: Mechanisms of environmental response	164
Charge transfer	166
Charge transfer with adsorbates.....	166
Charge transfer induced by UV irradiation	167
Mechano-structural changes	169
Water layer formation	171
Water accumulation at interfaces.....	171
Effects of water on ion mobility	172
Systems with mixed adsorption kinetics	173
Chapter 11: Future opportunities	176
Development of material expert system	177
Combinatorial synthesis robot.....	178
Simulations with real-time input.....	180
In situ diagnostics on X-ray and neutron beamlines	181
Chapter 12: Conclusions.....	184
References	187
Vita.....	225

List of Figures

- Figure 1. (a) Schematic of thin film-coated QCM crystal during analyte adsorption. (b) Example of crystal resonance shift during analyte adsorption. (c) Schematic of harmonic-dependent penetration depth of acoustic waves through an adlayer film. (d) Penetration depth (δ) of the acoustic wave in units of film viscosity (η) and density (ρ) as a function of crystal harmonic number. 11
- Figure 2. (a) Integrated multifunctional environmental system (IMES). (b) Schematic of IMES vacuum chamber. (c) Examples of portable sample environments used to complement IMES. (d) IMES enables characterization of materials across an ultra-broadband frequency range spanning electrical, gravimetric/viscoelastic, and optical functional modes.....15
- Figure 3. (a) Traditional materials characterization workflow in which most tasks are carried out manually by a human researcher using a variety of different software tools. (b) IMES employs custom integrated software which automates each process in the workflow and provides real-time feedback for iterative optimization of experimental conditions.....19
- Figure 4. The benefits of real-time analytics for spectroscopy data include (a) dynamic sampling window, (b) automated detection , tracking, and prediction of peak position, (c) multi-peak spectral deconvolution, (d) selective fitting of peaks of interest, (e) prediction of complete spectral response, and (f) real-time visualization of modeling results. 21
- Figure 5. AFM images of 25 nm thick and 100 nm thick (top and bottom rows, respectively) CuPc films deposited on glass substrates at 25°C, 150°C, and 250°C. Line profiles correspond to the bottom row of pixels in each image. Figure reproduced with permission.⁵⁷ 31
- Figure 6. Resistance response (R/R_0 , top panel) and mass change (ΔM , middle panel) of CuPc films during exposure to different pressures (bottom panel) of

H ₂ O vapor (blue colored pulses) and O ₂ (gray colored pulses). Films are labeled by their thickness (25 or 100 nm) and the temperature of the substrate during deposition (25°C, 150°C, or 250°C), with a generic name of XX nm, YY°C. Figure reproduced with permission. ⁵⁷	32
Figure 7. Normalized resistance change (R/R_0) during exposure to 20 Torr pulses of H ₂ O vapor (a) and O ₂ (b) for 1 hour. Normalized mass change (ΔM) in response to exposure of CuPc films to 20 Torr H ₂ O vapor (c) and O ₂ (d) for 1 hour. Figure reproduced with permission. ⁵⁷	34
Figure 8. The resistance change ($ \Delta R $) of 25 nm and 100 nm thick films during 1-hour exposure to 20 Torr pulses of H ₂ O vapor (a) and O ₂ (b) as a function of film deposition temperature. Figure reproduced with permission. ⁵⁷	36
Figure 9. (a) Total mass change (ΔM) in response to 20 Torr pulses of O ₂ (black) and H ₂ O (blue), shown for 25 nm and 100 nm thick films deposited at 25°C, 150°C, and 250°C. The inset is related to Figure 9(b). (b) Average time derivative of film mass (dM/dt) during O ₂ exposure (black) and H ₂ O exposure (blue) after initial rapid mass loading has occurred. dM/dt is extracted during O ₂ /H ₂ O exposure under isobaric conditions, highlighted in green in the inset of (a). For clarity, data from films deposited at 150°C are not shown since $dM/dt \approx 0$ g/s. Figure reproduced with permission. ⁵⁷	38
Figure 10. (a) AFM image of CuPcTs film. Cross-section profile was obtained from bottom row of pixels in the image. (b) H ₂ O adsorption isotherm (black circles) fit with five different isotherm models. The r^2 values of each fit are shown in the inset bar graph. Fit lines correspond to colors used in the bar graph. Error bars correspond to noise in the measured QCM signal. (c) Mass change (ΔM) (black, left axis) of CuPcTs film during exposure to pulses of H ₂ O vapor (blue, right axis). Red lines indicate examples of double exponential fits. (d) Ratio of double exponential fit parameters A_2/A_1 (black squares, left axis) and τ_2/τ_1 (red circles, right axis). Lines show linear fits. Error bars are propagated double exponential fitting errors. Figure reproduced with permission ⁵⁵	48

Figure 11. (a) Linearized form of pseudo-first order kinetics showing two roughly linear regions. (b) Reaction rate constants for first (k_{1-1}) and second (k_{1-2}) pseudo-first order kinetic processes identified in (a), shown with exponential fits. Error bars correspond to linear fitting errors. (c) Linearized form of the pseudo-second order kinetics showing highly linear behavior ($r^2 > 0.998$). (d) Top panel: comparison of *Site-2* occupancy (θ_2) as estimated from pseudo-first order kinetic and double exponential models. Bottom panel: percent difference ($|\Delta M_e|$) between measured equilibrium mass (M_e) and equilibrium mass predicted by pseudo-first order, pseudo-second order, and double exponential kinetic models. Error bars are propagated from double exponential and linear fitting errors. Figure reproduced with permission.⁵⁵ .51

Figure 12. (a) Wavelength-dependent extinction coefficient (k) (top panel) and index of refraction (n) (bottom panel) of CuPcTs film under different RH conditions. (b) Top panel: Optical film thickness as RH is increased (adsorption, black squares) and decreased (desorption, red circles). Lines show exponential fits. Error bars correspond to errors propagated from fitting to the Lorentz oscillator model. Bottom panel: Bandgap energy (E_g) of Q-band (left axis) and B-band (right axis). Straight lines show two roughly linear regimes. (c) Results from PCA analysis of Δ and (d) Ψ obtained from SPE measurements. RH dependence of principal components is shown in main plots with each component's contribution to the actual spectra shown in the insets. The units of Δ and Ψ are degrees and their principal components are displayed in relative units. Figure reproduced with permission.⁵⁵ 52

Figure 13. (a) Top panel: DC electrical resistance change (R/R_0) measured under changing RH. Red curve is exponential fit. Error bars correspond to uncertainty in R/R_0 due to low signal to noise ratio. Inset: equivalent circuit used to model EIS data. Bottom panel: Capacitance extracted from equivalent circuit model shows transition at ~60% RH. Error bars are propagated from errors in fitting to equivalent circuit model. (b) Relationship between optical conductivity (σ_{op}) and electrical conductivity (represented by

1/R, where R is the DC resistance), plotted with mass change (ΔM) of the CuPcTs film during uptake of water and an exponential fit (gray curve). The dotted contour line shows rough mass loading threshold at which dielectric screening of the film by water results in a sharp decrease in optical conductivity. Error bars are propagated from measurements of R/R_0 and extraction of ϵ_2 by fitting to the Lorentz oscillator model. Figure reproduced with permission.⁵⁵ 59

Figure 14. Water crowding at hydrophilic sulfonyl/salt groups leads to dissociation of Na^+ ions from $\text{Na}_4\text{CuPc}(\text{SO}_3)_4$. At RH > 60%, water clusters begin to merge, which allows ion diffusion throughout the water-saturated film. Mobile Na^+ ions are represented by purple (+) symbols while $\text{CuPc}(\text{SO}_3^-)_4$ ions are left with -4 charges. Figure reproduced with permission.⁵⁵ 63

Figure 15. (a) Estimated RH sensitivity achieved by measuring capacitance (C_1), DC resistivity (R/R_0), QCM frequency shift (ΔM), and optical constants (n) for RH sensing. Shaded regions represent uncertainty range. Right axes show estimated measurement sensitivity of each technique. Axes units are shown in plot legend. (b) Top panel: display of RH sensing limit of mass-based measurements showing ΔM as calculated from frequency shift of CuPcTs-coated QCM crystal (black) and bare gold-coated crystal (red). Bottom panel: Two pulses of H_2O vapor corresponding to ~0.15% RH which is detected using CuPcTs-coated QCM. Figure reproduced with permission.⁵⁵ 64

Figure 16. AFM images of (a) s-SWNT, (b) m-SWNT, and (c) MWNT networks. d. Schematic of photoinduced adsorption and desorption of electron-accepting O_2 and H_2O on CNTs. The energy barrier to electron transfer to (E_{A1}) and from (E_{A2}) the charge transfer complex ($\text{CNT}^{\delta+} \cdots [\text{acceptor}]^{\delta-}$) are decreased under UV irradiation, resulting in enhancement of both photoinduced chemisorption (1) and photoinduced molecular desorption (2). c. Schematic of H_2O adsorption and photoinduced desorption from a junction between two

bundles of (5,5) SWNT bundles on a gold-plated QCM crystal. Figure reproduced with permission.⁵⁹	72
Figure 17. (a) Mass change (ΔM) of CNT networks when exposed to 5, 10, 15, and 20 Torr pulses of O_2 in the dark and under UV irradiation. (b) ΔM when CNT networks are exposed to 5, 10, 15, and 20 Torr pulses of H_2O in the dark and under UV irradiation. (c) Resistance change (R/R_0) of CNT networks when exposed to pulses of O_2 in the dark and under UV irradiation. (d) Resistance change (R/R_0) of CNT networks when exposed to pulses of H_2O in the dark and under UV irradiation. In (c) and (d), $R/R_0 < 0.05\%$ for s-SWNT, m-SWNT, and MWNT networks in the dark. Figure reproduced with permission.⁵⁹	76
Figure 18. Change in mass (ΔM) of semiconducting SWNT (s-SWNT), metallic SWNT (m-SWNT), and MWNT networks when networks are exposed to a 20 Torr pulse of O_2 (a) and H_2O (b) in the dark (solid shapes) and under UV irradiation (open shapes). Introduction and removal of gas/vapor is marked by vertical dotted lines. Figure reproduced with permission.⁵⁹	78
Figure 19. Resistance change (R/R_0) of semiconducting SWNT (s-SWNT), metallic SWNT (m-SWNT), and MWNT networks when networks are exposed to a 20 Torr pulse of O_2 (a) and H_2O (b) in the dark (solid shapes) and under UV irradiation (open shapes). Introduction and removal of gas/vapor is marked by vertical dotted lines. Prior to the gas/vapor pulse, $R/R_0 < 0$ for metallic CNTs due to lack of full recovery from the previous pulse. Figure reproduced with permission.⁵⁹	81
Figure 20. Resistance response (ΔR) to O_2 (a) and H_2O (b) as a function of gas/vapor pressure in the dark (solid shapes) and under UV irradiation (open shapes). $\Delta R=0$ is denoted by the dotted horizontal line. Figure reproduced with permission.⁵⁹	83
Figure 21. (a) AFM image of PEDOT:PSS film at ambient humidity. (b) Cross-section of PEDOT:PSS film at 30%, 50%, and 93% RH. Average height of the film surface increases relative to the height of the tallest feature with	

increasing RH. Inset shows the cross section region. (c) Statistical analysis of the image in (b) at 30%, 50%, and 93% RH. Inset: skewness in the surface height distribution. (d) Mass change (ΔM , black open circles) and electrical resistance (solid blue squares) of PEDOT:PSS at different RH levels. Inset: average rate of change in mass ($\Delta M/\Delta RH$) and average rate of change in resistance ($\Delta R/\Delta RH$) as a function of changing RH levels. The units of $\Delta M/\Delta RH$ are [ng/%RH], and $\Delta R/\Delta RH$ units are [m Ω /%RH]. Figure reproduced with permission.⁵⁶ 92

Figure 22. (a) Surface potential of PEDOT:PSS film at 3%, 30%, 60%, and 93% RH. The image area is the same as that shown in Figure 21(b) inset. (b) Statistical analysis of KPFM images shown in (a). Average surface potential increases and the range of measured surface potential values decreases as water sorption leads to homogenization of the surface. Figure reproduced with permission.⁵⁶ 95

Figure 23. (a) Frequency-dependent real (Z') and (b) imaginary (Z'') impedance measured at 1 kHz, 500 kHz, and 1 MHz. (c) Equivalent circuit shunt resistance (R_s), ionic conduction resistance (R_{ion}), charge transfer resistance (R_{ct}), and (d) film capacitance (C_f) and film/electrode interface capacitance (C_e). Figure reproduced with permission.⁵⁶ 97

Figure 24. Rate of change in the optical bandgap (E_g) as estimated from spectroscopic ellipsometry. Units of $\Delta E_g/\Delta RH$ are in [eV/%]. Inset: optical thickness of PEDOT:PSS film as estimated from fit of SPE spectra. Error bars represent confidence limits estimated from MSE values of the fits. Figure reproduced with permission.⁵⁶ 100

Figure 25. (a) Wavelength-dependent optical conductivity (σ_{op}) extracted from imaginary dielectric constant measured at different RH conditions. (b) Strong correlation between optical conductivity (extracted at 550 nm) and electrical conductivity, represented by inverse of DC resistance ($1/R$). Figure reproduced with permission.⁵⁶ 103

Figure 26. (a) Cross-sectional bright-field TEM images of SU-8 film after 10 cycles of ZnO-infiltration synthesis, with the left panel showing a low-magnification, high-contrast view of the whole hybrid film and the right panel the upper portion of the film including the top dense layer at a higher magnification. (b) Intensity of ToF-SIMS peaks attributed to Cs_2OH^+ , Cs_2F^+ , C_2H_5^+ , Zn^+ , and Si^+ measured as a function of sputter time. Error bars represent the standard deviation between four different films. Sputter time is correlated to film depth, where 0 s corresponds to the film surface. (c) Profile of ToF-SIMS peak attributed to Zn^+ in films with 0, 4, 8, and 16 infiltration cycles. (d) Total Zn^+ counts, which is directly proportional to concentration of Zn in films, with 0, 4, 8, and 16 infiltration cycles. Figure reproduced with permission.²²⁶ 114

Figure 27. Normalized temporal frequency shift (Δf) of ZnO-infiltrated SU-8 films during exposure to (a) 22.6 Torr ($\sim 95\%$ RH) pulse of H_2O vapor and (b) 22.6 Torr pulse of O_2 . The data are normalized to $\Delta f = 0$ Hz at time = 0 s. Gas/vapor exposure and removal are marked by the vertical dotted lines. Numbers in legend correspond to number of ZnO-infiltration cycles and whether response was measured in the dark or under UV irradiation. (c) Frequency shift vs number of ZnO-infiltration cycles during exposure to H_2O and O_2 in the dark and under UV irradiation. Magnitudes shown in (c) are slightly higher than those in (a) and (b) because they were extracted from the absolute frequency shift²²⁶. (d) Percent change in frequency shift ($|\Delta f_{\text{UV}}|$) between films exposed to gas/vapor in the dark and those measured under UV irradiation. Left and right axes show differences in frequency shift when films were UV irradiated during exposure to H_2O vapor and O_2 , respectively. Figure reproduced with permission.²²⁶ 118

Figure 28. (a) Contact angle of water droplet measured on SU-8 films with 0, 4, 8, and 16 ZnO-infiltration cycles in the dark and under UV irradiation. Inset shows representative images of droplets in the dark (top) and under UV irradiation (bottom). Contact angles were measured after 2 min of droplet

formation. (b) Histograms of contact potential difference (VCPD) measured using KPFM in the dark and under UV irradiation for eight cycle ZnO (black) and eight cycle ZnO-infiltrated SU-8 (red). Figure reproduced with permission.²²⁶ 121

Figure 29. (a) Frequency shifts of ZnO-infiltrated SU-8 films after 80 min of H₂O (top panel) and O₂ exposures (bottom panel) at different gas/vapor pressures and illumination conditions (dark or UV). RH corresponding to each H₂O vapor pressure is shown on top horizontal axis. The solid lines correspond to fits to the Toth isotherm. Error bars correspond to noise signal in frequency shift measurements. (b) Corresponding Toth isotherm constants (K_T , top panel) and Toth exponents (t , bottom panel) extracted from Toth isotherm fits in (a). Note the use of logarithmic scale in top panel. Error bars correspond to uncertainties propagated from noise signal in frequency shift measurements. Figure reproduced with permission.²²⁶ 123

Figure 30. (a) Estimated detection limits for O₂ (top panel) and H₂O vapor (bottom panel) sensing using ZnO-infiltrated hybrid SU-8 films. The left vertical axes correspond to O₂/H₂O partial pressures, and the right vertical axes O₂ partial pressure in units of % P/P_0 (where P_0 is partial pressure of oxygen in atmosphere, ~160 Torr) (top) and % RH at 27°C (bottom). Note the use of log scales. The yellow shaded region corresponds to the control ALD ZnO films, the gray region to ZnO-infiltrated SU-8 films in the dark, and the white to ZnO-infiltrated SU-8 under UV irradiation. The numbers on horizontal axis correspond to the number of ZnO-infiltration synthesis cycles. Error bars correspond to amplitude of noise in frequency shift measurements. (b) Time constant (τ) measured from frequency shift during the adsorption of H₂O/O₂ in the dark and under UV irradiation. Figure reproduced with permission.²²⁶ 128

Figure 31. (a) DC electrical resistance of control ALD-mode-prepared ZnO films and ZnO-infiltrated hybrid SU-8 films measured in the air in the dark as a function of the number of infiltration synthesis cycles. The ZnO-infiltrated

SU-8 film with 0 infiltration cycle corresponds to the un-infiltrated SU-8 film. (b) DC electrical resistance change (ΔR_{UV}) after 10 min of UV irradiation for control ZnO films and ZnO-infiltrated hybrid SU-8 films. Figure reproduced with permission.²²⁶ 131

Figure 32. (a) Top panel: Fundamental frequency shift (Δf , left axis) of Ti_3C_2 -coated QCM and bare Au-coated QCM during exposure to water vapor partial pressures spanning over 3 orders of magnitude (bottom panel). Right axis of top panel shows DC electrical resistance change (ΔR) of Ti_3C_2 film. Water concentration in bottom panel is shown in terms of relative humidity (RH) and H_2O vapor pressure. (b) Fundamental frequency shift (black, left axis) and electrical resistance change (blue, right axis) measured from 0-95% RH after 3 hours of exposure to each RH level. (c) Frequency shift and resistance change during exposure to single H_2O vapor pulse (bottom panel) corresponding to ~ 25 mTorr H_2O vapor pressure (0.1% RH). Solid dark lines show response after 50-point adjacent averaging. Figure reproduced with permission.²⁶⁷ 139

Figure 33. (a) Impedance (Z) of Ti_3C_2 film measured at 100 Hz during exposure to 0, 5, 20, 40, 60, 80, 95% RH (blue, right axis). (b) Nyquist representation of impedance of Ti_3C_2 film (black points) fitted to double RC equivalent circuit (blue line). Inset shows equivalent circuit model composed resistance and capacitance in bulk grains (R_G, C_G), resistance and capacitance at grain boundaries (R_{GB}, C_{GB}), and resistance at contacts (R_c). (c) Values of R_{GB} and R_G extracted from equivalent circuit fits. (d). Values of C_{GB} and C_G extracted from equivalent circuit fits. Error bars correspond to uncertainty introduced during fitting of equivalent circuit model. Figure reproduced with permission.²⁶⁷ 142

Figure 34. (a) Change in current (ΔI) measured across Ti_3C_2 film under 3 mV DC bias. Gray points show measured current, black line shows current after smoothing by 50-point adjacent averaging. Blue pulses (right axis) correspond to 0, 40, and 95% RH. (b) Current change showed roughly

double exponential trend with RH (blue line). Error bars represent amplitude of noise in current signal. Inset: Ti_3C_2 film showed linear current-voltage characteristics from -1 to 1 VDC bias. Figure reproduced with permission.²⁶⁷

.....144

Figure 35. (a) Frequency shift normalized to harmonic number ($\Delta f/n$) of Ti_3C_2 -coated QCM during exposure to increasing RH levels (blue, right axes). Values of $\Delta f/n$ for bare Au QCM were subtracted to remove effects of water adsorption on Au and drag forces arising from changing density and viscosity of humid air. Legend shows crystal harmonic number. (b) Gravimetric sensitivity of Ti_3C_2 film to humidity estimated as a ratio of normalized frequency shift of 1st, 3rd, 5th, 7th and 9th harmonics over change in RH%. Figure reproduced with permission.²⁶⁷ 146

Figure 36. Sensitivity of Ti_3C_2 humidity sensing modalities. Normalized sensitivity = S/S_{max} , where S is sensitivity and S_{max} is maximum sensitivity achieved for a given sensing mode. Figure reproduced with permission.²⁶⁷ 148

Figure 37. (a) Normalized resistance change (R/R_0) of K- and Mg-intercalated MXenes during exposure to water vapor. H_2O pressure (P/P_0) is shown in lower panel, where P_0 is the H_2O saturation pressure at 27 °C (~23.8 Torr). (b) Normalized frequency shift (Δf) under the same RH conditions. For reference, frequency shift of a bare Au-coated crystal is shown in red. (c) Changes in ΔR and ΔM (film mass) as a function of P/P_0 shown with corresponding exponential fits. (d) Changes in ΔR as a function of ΔM are shown with corresponding linear fits. Figure reproduced with permission.³⁸ 157

Figure 38. (a) Exponential time constant (τ) for ΔR and ΔM responses during H_2O desorption. Note break in y-axis. (b) Comparison of average value of τ in Ti_3C_2 -K and Ti_3C_2 -Mg. Figure reproduced with permission.³⁸ 160

Figure 39. (a) Normalized resistance change upon exposure to 10^{-3} Torr vacuum after MXene films were exposed to air. (b) Normalized mass change of

MXenes as a function of temperature. Derivative of mass with respect to temperature is shown in inset. Figure reproduced with permission.³⁸.....162

Chapter 1: Introduction

This study describes a workflow for high-throughput characterization of multifunctional response of materials to their environment. The first chapter describes motivation for the work in the context of broader themes in science and engineering. Chapter 2 provides general information about experimental methods, instrumentation and software utilized in subsequent chapters. Chapters 3 – 9 are composed of published studies related to the environmental response of functional materials, including organic small molecules, nanotubes, polymers, and 2D materials. For readers who wish to read a single chapter based on its relevance to a specific material, Chapters 3 – 9 are meant to function as stand-alone studies so some text is repeated for clarity. Chapter 10 describes common mechanisms of material response to environment and describes correlations between the response of different materials. Chapter 11 discusses potential research opportunities for future development of the workflow established in this study. Chapter 12 offers conclusions about the work.

Background and motivation

Advances in thin film synthesis, multilayer patterning, and 3D micro-additive manufacturing have enabled the development of a broad range of emerging technologies with unprecedented functionality and portability, including low-cost sensors for internet of things (IoT) networks, smart textiles, flexible displays, microelectromechanical systems (MEMS), and lab-on-a-chip diagnostic biomedical devices¹⁻³. Future improvements in device functionality and miniaturization will be primarily driven by design, discovery and deployment of novel materials⁴⁻⁶ using combinatorial methods and machine learning⁷⁻¹⁰ with guidance from comprehensive materials databases¹¹⁻¹⁴ such as those assembled by the Materials Genome Initiative¹⁵.

Although discovery and design of materials has been accelerated by high-performance computing, wide availability of data, and automated synthesis techniques, testing of material functionality generally requires human-based intervention and remains labor-intensive and reliant on experienced researchers¹⁶⁻¹⁷. Characterization of functional properties and assessment of long-term film stability are often the most challenging steps to automate in the materials characterization workflow¹⁸ and represent a primary bottleneck in the roughly 20-year process from materials discovery to commercial deployment¹⁷⁻¹⁹. Automated sample characterization remains challenging due to the broad range of functional film materials which must undergo screening (e.g. nanoparticles, nanotubes, two-dimensional materials, polymers, ionic liquids, and oxides), and use of a wide variety of chemical (e.g. chemical vapor deposition, atomic layer deposition) and physical (e.g. spin-coating, sputtering, pulsed laser deposition) deposition techniques which results in significant heterogeneity between samples.

Stand-alone off-the-shelf instruments are generally unsuitable for high-throughput materials testing because they lack the flexibility to accommodate different sample geometries, specific experimental procedures, and customized batch data processing routines. Efficient multi-functional material characterization requires a dedicated in-situ diagnostics system which allows simultaneous probing of multiple film functionalities²⁰ and provides capabilities for simultaneous multi-sample testing and control of ambient environmental conditions, including pressure, temperature, humidity, and light intensity, for assessing the environmental response and long-term stability of functional films.

Precise control of ambient environment is critical for reproducible thin film characterization. The poor electrical and morphological stability of many functional thin film materials limits their suitability for adoption in commercial or industrial applications. Due to their nanometer-micrometer scale thicknesses and

inclusion of patterned microstructures, low-dimensional materials, and microporous materials, functional thin films often exhibit surface area to volume ratios which are significantly higher than those of corresponding bulk materials. This leads to functional mesoscale behavior which is dominated by surface and interface effects rather than bulk properties, resulting in materials which are highly susceptible to interaction with the ambient environment.

Film stability is particularly important in the context of emerging organic electronics and low-dimensional materials. Functional organic films offer promising alternatives to traditional silicon-based device components because of their low cost, mechanical flexibility, and compatibility with solution-based processing, which enables low-cost large-area flexible technologies including organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic thin film transistors (OTFTs), and a wide range of organic thin film bioelectronics and sensors²¹⁻²⁴. Conjugated polymers, graphene, carbon nanotubes and phthalocyanines rely on delocalized π -systems for charge transport²¹ which promotes thermodynamic stability but often results in strong reactivity with oxidizing species like oxygen and water. Long-term stability of organic materials is often limited by their rate of oxidation, which can lead to loss of conjugation, decreased charge carrier density, and introduction of electronic scattering sites^{22, 25-26}. Under typical thermodynamic condition, material surface energy decreases during adsorption of gas or vapor molecules, resulting in chemical doping which can compromise electronic stability²⁷. Thermal fluctuations and incident radiation can result in additional chemical and electronic doping, polymer chain scission, and photobleaching.

While thin film interaction with ambient environment adds complexity to functional materials characterization, design of environmentally-responsive thin films is crucial for development of sensor technologies for IoT devices, autonomous vehicles, industrial process control, environmental monitoring, and biomedical

applications²². Chemical sensing comprises an important functionality for many nanomaterials and functional organic materials because of their high surface areas and strong response to gas/vapor and light. Typical commercial gas sensors rely on metal oxide films which require elevated temperatures for maintaining sensor reversibility. In contrast, thin film sensors based on conducting polymers and small organic molecules are often deposited at room temperature by simple solution-based deposition or printing, which significantly lowers the cost of sensor fabrication. Polymer-based chemical sensors may be operated at room temperature, which increases sensor portability and decreases energy requirements associated with sensor operation²⁸. In addition, analyte sensitivity can often be tuned by modifying film polymerization or chemical functionalization²⁹.

Current challenges

Precise control of ambient environment is critical for characterizing the stability of functional materials. For rapid testing of material response, novel high-throughput methods which accommodate batch sample processing and automated probing of multiple film functionalities are needed. However, implementing an environmentally-controlled platform for efficient high-throughput materials characterization remains challenging. This section discusses primary challenges related to experimental design and data processing.

The first challenge is associated with manual experiment planning. Appropriate design of experiment (DOE) strategy is critical for unfolding complex relationships between multiple experimental parameters, particularly for lengthy experimental workflows in which experimental conditions must be optimized prior to initiation of the experiment³⁰⁻³¹. Manual human-based experiment planning remains a primary roadblock for efficient DOE for multi-functional materials

characterization due to the potentially-large number of measured parameters, dynamic environmental conditions, and instrument settings.

Before initiating an experiment to test material response to environment, a sequence of environmental testing conditions must be manually designed and entered in experimental control software to allow for automated temporal control of temperature, ambient pressure, relative humidity, analyte gas/vapor flow, and intensity of auxiliary light sources. Design of experimental conditions becomes particularly complex during multi-sample testing due to variation in the environmental sensitivity, response time, and reversibility of different samples. Exploration and design of a multi-dimensional environmental parameter space, which for example may be represented as a multi-dimensional grid of varying pressure, temperature and humidity, requires further complexity and significantly increases the duration of experiments and need for human-led planning and preparation. Along with selection of appropriate environmental testing conditions, a broad range of measurement parameters and instrument settings must be determined and set manually prior to each experiment. Important measurement settings which must be selected by an experienced researcher include current-voltage (I-V) and cyclic voltammetry (C-V) scanning directions, step sizes, and sweep rates, AC and DC bias voltages, frequency ranges, sampling rates, and integration times for impedance spectroscopy and acoustic gravimetric measurements. Challenges associated with manual experiment tuning highlight the need for automated optimization of experimental conditions and measurement settings which allow increased experimental throughput due to a reduction in redundant experimental procedures and time spent by human researchers for manual adjustment of experimental settings.

The second major challenge related to automation of high-throughput film characterization is associated with data processing, analysis and modeling. Simultaneous acquisition of electrical, optical, and gravimetric measurements

results in a complex data stream which may contain channels consisting of one-dimensional (e.g. time-dependent electrical resistance), two-dimensional (e.g. frequency-dependent electrical impedance spectra), or higher-dimensional (harmonic-dependent multi-frequency QCM impedance spectra) data. Experiments running concurrently may require different integration times for different instruments, resulting in final output data which contains inconsistent time-referenced indices. Across different characterization modes and output file formats, data must be efficiently timestamp-referenced to enable matching of thin film response to the specific environmental conditions present at the time of acquisition. Analysis of output data from multiple instruments with different file formats generally requires manual intervention and post-processing by an experienced human researcher. However, manual post-processing of data often cannot occur until after completion of an experiment and may require hours or days depending on the number of samples, measurement techniques, and size of the environmental parameter space which was probed. After initial data processing and analysis, a preliminary understanding of sample response may be formulated. Preliminary results often shed light on flaws in the experimental design such as suboptimal instrument settings or poor sampling of environmental conditions of interest. Experimental design can then be improved in a follow-up experiment, but this iterative process is prohibitively labor-intensive and time-consuming. After appropriate experiments are designed and deployed, formal data analysis and physical modeling may require hours or days. The time-consuming process of manual post-experiment data organization, formatting, analysis, and modeling represents a critical bottleneck in the high-throughput experimental workflow.

The benefits of combinatorial materials synthesis and data-driven materials design will not be fully realized unless novel materials can be rapidly screened for stability and functionality under a broad range of ambient environmental conditions. The ideal platform for rapid characterization must enable

simultaneous probing of different material functionalities (e.g. electrical, optical, gravimetric, viscoelastic), accommodate high-throughput batch sample measurements, provide control of ambient environment conditions (e.g. temperature, pressure, humidity, gas/vapor composition, light intensity), and offer flexible software which automates experimental procedures and data processing. These capabilities are not possible on off-the-shelf commercial systems. The lack of a suitable system forms the primary motivation for this study, which is to create an automated high-throughput multi-functional characterization platform. The remainder of this study describes details of the platform and provides examples of functional materials which were characterized using the platform. Finally, opportunities for future development of the system are provided as a roadmap for future researchers.

Chapter 2: Experimental methods and workflow

This chapter describes building blocks of the materials characterization platform and associated workflow, including instrumentation and analytical methods related to the quartz crystal microbalance, the environmental sample chamber, and the custom control and analysis software which was designed to mitigate challenges described in the previous chapter.

Quartz crystal microbalance

Acoustic sensors are commonly used as transducers for detection of gas sorption on materials of interest. One of the most widely used bulk acoustic wave sensors is the quartz crystal microbalance (QCM), which consists of an AT-cut piezoelectric quartz crystal and an electronic resonator which drives thickness shear-mode oscillations in the crystal. Monitoring the behavior of mechanical resonances in the crystal enables characterization of gravimetric and viscoelastic changes in a thin film adlayer deposited on the crystal surface (Figure 1(a)). The QCM has found widespread use in scientific and industrial applications including thin film processing, environmental monitoring, machine olfaction and biomedical sensing due to its sub-nanogram mass sensitivity and versatility under gas, vacuum, and liquid environments³²⁻³⁴.

A solid adlayer film deposited on the quartz resonator has complex shear modulus $\mu^* = \mu' + i\mu'' = \mu + i\omega\eta$, where the real part (storage modulus) corresponds to elasticity (μ) and the imaginary part (loss modulus) corresponds to viscous loss (η)³⁵. As described by Sauerbrey³⁶, a QCM coated by a uniform rigid film ($\eta = 0$) undergoes resonance frequency shift (Δf_n) at the n^{th} crystal harmonic in response to a change in the film mass (Δm) by an amount $\Delta f_n = nC\Delta m$, where n is the harmonic number and C is a constant related to physical properties of the quartz resonator. The fundamental ($n = 1$) frequency shift can

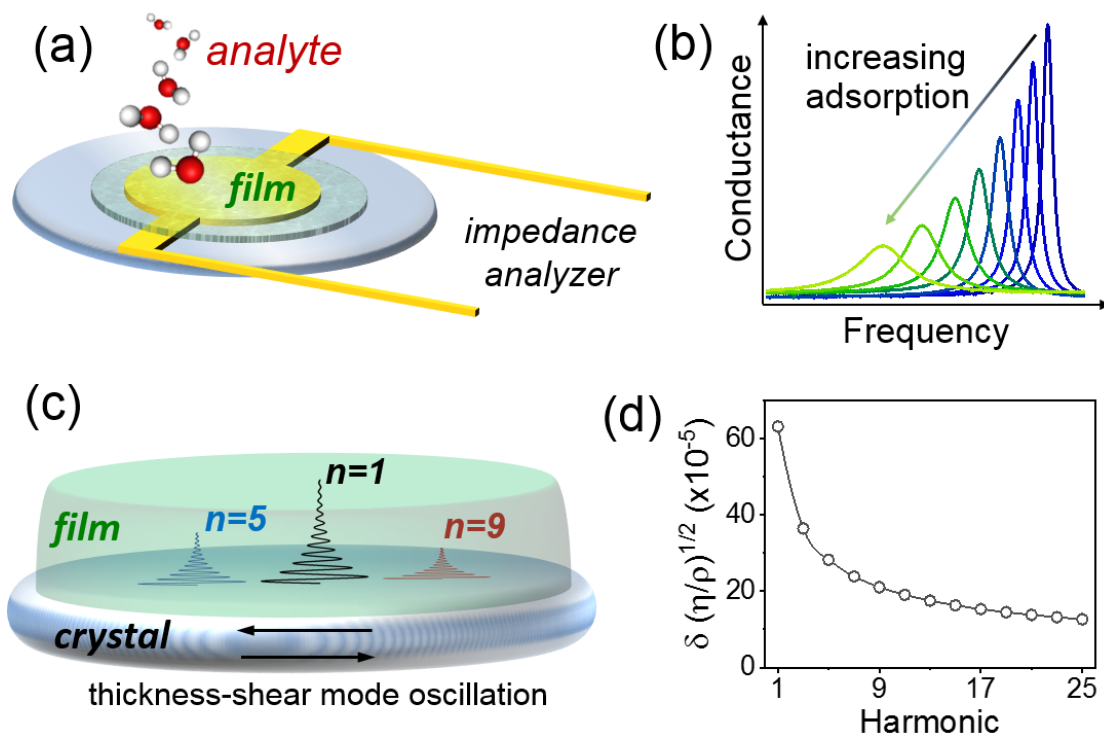


Figure 1. (a) Schematic of thin film-coated QCM crystal during analyte adsorption. (b) Example of crystal resonance shift during analyte adsorption. (c) Schematic of harmonic-dependent penetration depth of acoustic waves through an adlayer film. (d) Penetration depth (δ) of the acoustic wave in units of film viscosity (η) and density (ρ) as a function of crystal harmonic number.

be measured using low-cost Pierce oscillator circuits (~\$75), enabling single-frequency gravimetric characterization of thin rigid adlayers³⁷⁻³⁸.

In the case of soft adlayers ($\eta > 0$), viscous shear in the film dissipates energy of the acoustic wave during oscillation, which introduces nonlinearity to the relationship between Δf and Δm . Gravimetric/viscoelastic modelling of soft films requires knowledge about changes in the amount of dissipated energy (ΔD , which is related to quality factor of the resonance peak) in addition to the resonant frequency shift^{35, 39}. Several commercial QCM systems (~\$3000) feature dissipation monitoring (QCM-D) at only the fundamental resonant frequency⁴⁰ (Figure 1(b)). However, when higher crystal harmonics are observable, the fundamental resonant frequency (Δf_1) is often neglected due to its low signal to noise ratio (SNR) since Δf_n scales linearly with n ⁴¹⁻⁴³. Measurement at higher ($n > 1$) harmonic resonances improves sensitivity and enables spatially-controlled probing of the adlayer (Figure 1(c)), as penetration depth of the acoustic wave into the film is proportional to $n^{-1/2}$ (Figure 1(d)).⁴⁴ Monitoring frequency shift and energy dissipation at multiple harmonics generally requires frequency-dependent measurement of the crystal impedance by a network analyzer. Commercial systems which feature multi-harmonic QCM-D (>\$10000) are often prohibitively expensive and lack versatility due to large flow cell size, specific crystal-mounting geometries, and locked proprietary software.

High frequency resonators often produce inharmonic resonances of the fundamental vibration modes. These spurious modes may be isolated or mechanically coupled to the fundamental modes. Spectral analysis by commercial QCM-D systems is often limited to small (~2 kHz) frequency windows near the primary odd crystal harmonics in order to avoid interference from spurious modes, which may lie close enough to main resonance peaks to be considered distortions of the resonance peaks, or far enough away from the resonance peaks to be considered distinct spurious overtone peaks⁴⁵. During

large changes in resonant peak position or intensity, lock-in electronics in commercial systems often lose the position of harmonic peak and begin tracking the position of an undesirable spurious mode, causing discontinuous jumps in measured impedance spectra⁴⁶⁻⁴⁷. To avoid this, spurs are often fitted separately from main resonance peaks and removed by subtraction⁴⁸ or disregarded completely⁴⁹. The separation between spurious resonances and main harmonic peaks decreases with harmonic number, leading to significant distortion and coupling of spurs to resonant peaks at high harmonics^{46-47, 50}. For cases in which the quality factor of a spurious peak is higher than that of the harmonic peak, tracking of the spurious peak position yields higher sensitivity in frequency shift measurement than does tracking of the harmonic peak. Commercial QCM-D systems generally monitor Δf and ΔD at the main harmonic modes, but lack flexibility required for tracking parameters of the inharmonic spurious modes, which limits SNR and frequency shift sensitivity when spurious are sharper than the fundamental peak. Utilization of spurious overtone peaks is only possible by broad-range (>10 kHz) measurement of impedance spectra. This is generally not possible using locked proprietary software, which highlights the benefits of using custom software and electronics for QCM control.

Values of Δf and ΔD measured at multiple crystal harmonics provide the basis for a variety of models which enable estimation of physical properties of films deposited on the QCM surface. Analytical models have been constructed for understanding behavior of a broad range of adlayer films and media, including rigid films³⁶, porous coatings⁵¹⁻⁵², viscoelastic films³⁵ and fluids⁵³. In addition, QCM response of adsorbent films with heterogenous properties may be modeled by finite-element methods⁵⁴, continuum mechanical approaches³⁵, or two-fluid models⁵³ which approximate inhomogeneous viscoelastic film as a stack of two disparate viscous fluids. Models used for analysis of QCM data are described in detail in subsequent chapters. When used in conjunction with electrical or optical film characterization, modeling of QCM response enables coupling of functional

film properties to gravimetric/viscoelastic response during gas/vapor adsorption, providing valuable insight into the effects of environment on functional film behavior⁵⁵⁻⁵⁸. This simultaneous multimodal structural-functional characterization often requires flexibility in crystal mounting geometry, flow cell design, and portability of electronic components. These requirements establish constraints which are not satisfied by most low-cost commercially available QCM platforms, which often employ locked proprietary software which does not accommodate custom experimental protocols. To circumvent these constraints, we employ a portable low-cost antenna analyzer (~\$360) for use in measuring full crystal conductance spectra which enables multi-overtone QCM-D. The low cost portable QCM-D system allows identification and tracking of overtone peaks up to the 31th crystal harmonic and exhibits SNR and sensitivity comparable to a leading commercial system, enabling gravimetric and viscoelastic characterization of a broad range of soft and rigid films with thicknesses from 10s of nm to 10s of μm .

Integrated multifunctional environmental chamber

Direct coupling of QCM measurements to electrical and optical response of materials remains challenging. To address challenges related to high-throughput materials characterization under controlled environment, an integrated multifunctional environmental system (IMES) was developed at the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) (Figure 2(a)). The system enables multimodal film characterization inside a vacuum chamber while a two-gas mixing system delivers gas/vapor compositions at controlled pressures and flow rates (Figure 2(b)). The gas injection system performs automated delivery of precise gas/vapor analyte conditions and relative humidity (RH) by mixing O₂, H₂O, CO₂, N₂, Ar, or H₂ + Ar. Temperature is controlled by a heating plate mounted inside the chamber with

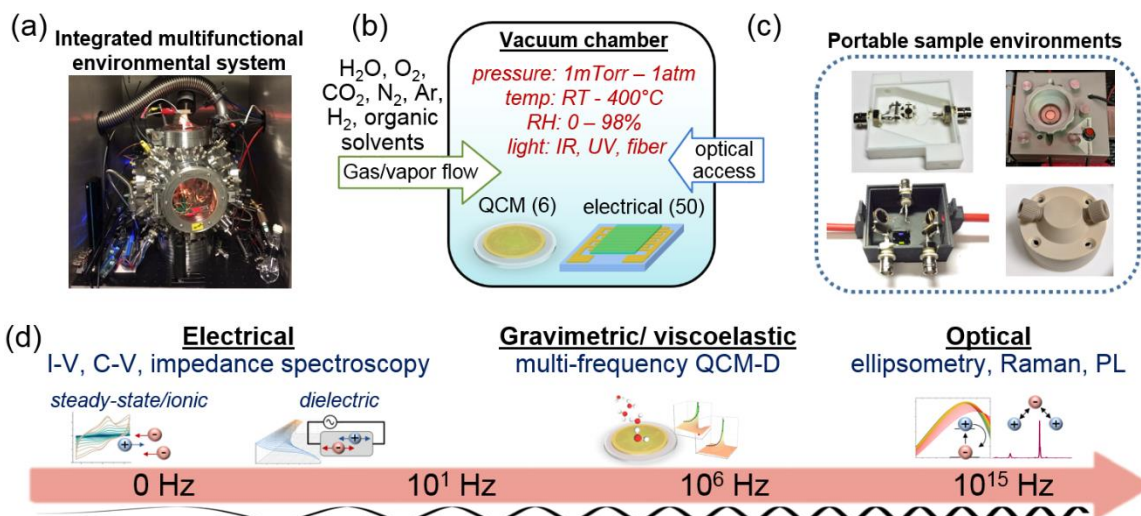


Figure 2. (a) Integrated multifunctional environmental system (IMES). (b) Schematic of IMES vacuum chamber. (c) Examples of portable sample environments used to complement IMES. (d) IMES enables characterization of materials across an ultra-broadband frequency range spanning electrical, gravimetric/viscoelastic, and optical functional modes.

embedded thermocouples. A quartz optical window allows for sample heating and surface activation by infrared (IR) and ultraviolet (UV) light sources mounted outside the chamber. The system is equipped with vacuum feedthroughs containing over 50 channels for electrical connections, enabling impedance spectroscopy, I-V, C-V, and back-gating transistor measurements on multiple samples simultaneously. Additional electrical channels are dedicated to multi-harmonic quartz crystal microbalance with dissipation monitoring (QCM-D) for multi-sample gravimetric and viscoelastic measurements. Two optical fiber feedthroughs provide one channel for optical diagnostics. The combination of DC electrical measurements (0 Hz) with electrical impedance (mHz – MHz), multi-frequency QCM (MHz – 100 MHz), and optical diagnostics (THz) enables multi-functional film characterization across an ultra-broad frequency range (Figure 2 (d)). Pumping the chamber to 10^{-5} Torr vacuum before and after measurements allows environmental response to be referenced to film behavior under vacuum, enabling clear differentiation between intrinsic film behavior and that resulting from doping by gas/vapor molecules. For coupling vacuum-based response to material behavior at ambient pressures and liquids, a set of portable environmental flow cells was designed, and 3D printed and integrated into the experimental workflow (Figure 2(c)). The auxiliary flow cells enable compatibility between in situ QCM and electrical measurements and spectroscopic ellipsometry, Raman spectroscopy, photoluminescence, atomic force microscopy (AFM), electrochemistry and laser scanning confocal microscopy. Data acquisition and control of source-measure units, QCM electronics, optical spectrometers, and environmental conditions inside the measurement cells are controlled through central dedicated LabVIEW and Python user interfaces, which allow real-time display of measured data and automated control of environmental conditions. The IMES system has been successfully used to investigate multi-functional environmental response of broad range of thin film materials including carbon nanotubes⁵⁹, MXenes^{38, 60}, conjugated polymers^{40, 56}, organic

semiconductors^{40, 55}, polymer-nanotube composite films³⁷, perovskites⁶⁰⁻⁶¹, proteins⁶² and metal oxides^{58, 63}.

Integrated control and analysis software

Some of the challenges associated with high-throughput materials characterization described in the previous chapter may be mitigated by incorporation of computer-based decision-making and real-time data analytics into experimental control software. Machine learning (ML) and algorithmic-based methods for control of data acquisition and processing procedures have shown enormous promise for increasing efficiency of functional materials screening⁶²⁻⁶⁵. Authors of a 2018 Materials Acceleration Platform (MAP) report concluded that their primary research goal was to create and deploy laboratories that “autonomously design, perform, and interpret experiments”⁶⁶. Computer-controlled experiments show potential for reducing redundancies in sequential human-designed experiments and can complement labor-intensive planning by human researchers. Combining in situ data analytics with computer-based planning allows automated transmission of feedback to experimental control systems, enabling iterative experimental design based on real-time response of samples under test. Experiments which incorporate fully-automated in situ data analytics allow researchers to observe model parameter evolution in real-time, enabling rapid hypothesis formation and assessment which reduces the need for lengthy data post-processing after experiment completion. Additionally, researchers have access to unexplored benefits of mixed-mode analytics in which material properties spanning multiple functional modes may be viewed simultaneously. Recent studies have demonstrated highly-automated workflows for characterization of material growth rate¹⁷, microstructure⁶⁷⁻⁶⁸, mechanical properties⁶⁹, and surface area⁷⁰, but computer-controlled multifunctional characterization remains challenging.

To supplement traditional analytical and statistical models, a variety of regression-based ML algorithms including artificial neural networks (ANNs), random forests (RFs), and support vector machines (SVMs) may be used to enable more accurate modeling and prediction of nonlinear multi-dimensional data. ML has been successfully applied to materials science in fields of materials design and discovery^{7, 71} and microscopy⁷² and has been implemented in post-processing of data streams produced during IMES-based experiments for gas discrimination and materials identification³⁷, biomolecule classification⁶², deconvolution of pressure and humidity⁴⁰, and classification of ambient environmental conditions⁶³. However, most ML algorithms require lengthy pre-processing procedures which limits their suitability for applications demanding real-time model creation and deployment. For full advantages of ML-based analytics to be realized, including real-time prediction of material response, preprocessing and modeling of data must be performed in situ using automated routines.

In traditional materials characterization workflows, an experienced human researcher must manually select instrument settings and experimental conditions (Figure 3(a)). Data is then acquired in automated experiments which may take minutes to days to complete using software specifically-designed for control of laboratory instruments. This software is typically proprietary and either ships with the instruments or includes a set of drivers in a customizable graphical interface tool like National Instruments LabVIEW. After experiment completion, the researcher often uses different software tools for data processing, analysis and modeling, which is often a scripting language with access to libraries for scientific computing and numerical analysis like Python, MATLAB or R. After analysis of data, results are often visualized and displayed in publication-quality images using specialized plotting software like Origin. Once the final conclusions are appropriately displayed and interpreted by researchers, they can be used as input for future experiments, resulting in a workflow which is inefficient and time-

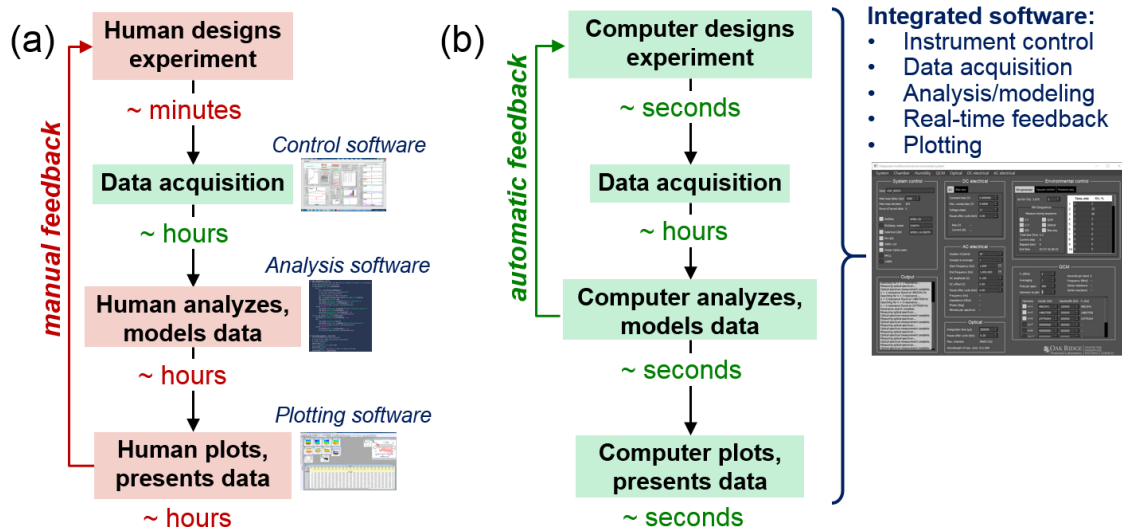


Figure 3. (a) Traditional materials characterization workflow in which most tasks are carried out manually by a human researcher using a variety of different software tools. (b) IMES employs custom integrated software which automates each process in the workflow and provides real-time feedback for iterative optimization of experimental conditions.

consuming because of the common use of multiple software tools and need for manual human intervention.

The IMES system is designed to improve workflow efficiency by reducing experimental redundancies and minimizing researcher input. Custom IMES software integrates DOE, data acquisition, data processing and analysis, and plotting in a central codebase (Figure 3(b)). The IMES control software is written in Python and uses the Qt framework to provide a cross-platform graphical user interface (GUI), enabling rapid DOE and automated data acquisition from a wide range of characterization instruments. Primary advantages of IMES software lie in on-line data processing capabilities, which enables real-time analysis of experimental data for use as feedback to the system to allow iterative optimization of the DOE.

Benefits of real-time data processing in the IMES control software are best demonstrated in terms of QCM response because of its multi-dimensional spectral output, dynamic peak behavior and applicability to a variety of complex physical models. Figure 4 describes examples of the benefits of on-line analysis for processing of QCM data. Conductance spectra are smoothed using a second-order univariate spline fit to increase SNR, then peaks in the smoothed spectra are detected using a custom peak-detection algorithm based on the second derivative of the conductance. For equivalent electrical circuit modeling of the resonance peaks, spectra are fitted to the Butterworth Van Dyke (BVD) resonator circuit model⁵⁰, which yields values of position, width, and equivalent RLC values associated with each resonant peak. Peak position and width calculated at each crystal harmonic are used for adjusting bandwidth of the measured frequency range, enabling a self-learning, iterative, dynamic frequency window which tracks position of the resonant peak and ensures that tails of the peak are not truncated due to shifts outside of the measured frequency window (Figure 4(a)). The optimal frequency band is predicted by extrapolating from an array of previously

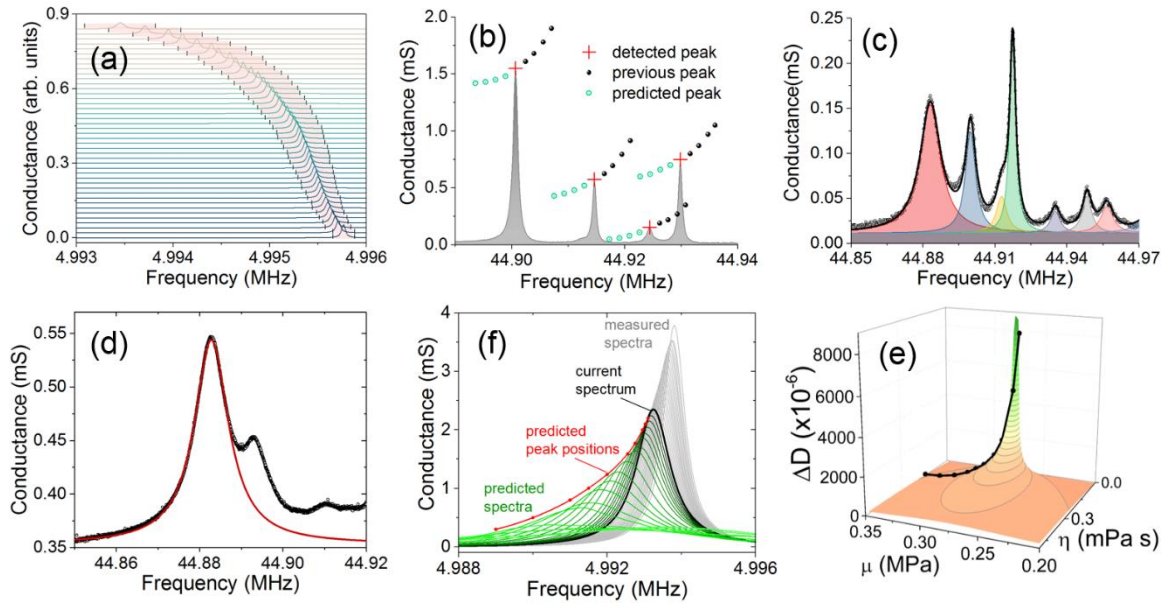


Figure 4. The benefits of real-time analytics for spectroscopy data include (a) dynamic sampling window, (b) automated detection , tracking, and prediction of peak position, (c) multi-peak spectral deconvolution, (d) selective fitting of peaks of interest, (e) prediction of complete spectral response, and (f) real-time visualization of modeling results.

detected peak positions (Figure 4(b)). Multi-peak fitting and deconvolution of conductance spectra (Figure 4(c)) allow subtraction of contributions from auxiliary spurious overtone peaks, enabling a selective-fitting procedure which ensures that the shape of the main peak fit is not distorted by the presence of spurious modes (Figure 4(d)). Once the trajectory of each resonance peak and associated spurious overtone peaks is calculated, the entire spectral response can be predicted (Figure 4(e)) to enable accurate estimation of the initial conditions for peak deconvolution. Finally, deconvoluting and fitting of spectral response in real time enables fit parameters to be used for development of physical models of the material response (Figure 4(e)). Changes in peak position (Δf) and peak width (ΔD) of QCM resonances are used as inputs for estimating film shear modulus (μ), viscosity (η) and density (ρ) using the continuum mechanics approach formulated by Voinova and coworkers³⁵.

Results from on-line analysis of QCM response are used as feedback for iterative optimization of measurement settings. Peak intensities and baseline conductance are used to estimate SNR of the QCM conductance spectra. The SNR is used as feedback to the central control software for adjustment of integration time and sampling rate. For autonomous control of environmental conditions during the experiment, changes in positions and widths of the resonant peaks at each crystal harmonic are used to calculate the derivative of BVD model parameters with respect to changes in ambient environment (i.e. temperature, pressure, relative humidity). Environmental conditions which result in the most significant spectral response are identified and used as feedback for the control software so that they can be re-sampled at higher resolution to efficiently capture details in the dynamics of film response.

Alongside QCM measurements, concurrent electrical characterization is often carried out using electrical impedance, I-V, and C-V techniques. Maximum sweep voltage is determined automatically based on measured film current and

rate of change of current with respect to applied voltage. For impedance measurements, frequency range and applied AC bias are determined by measured sample impedance and SNR in impedance spectra. Electrical impedance data is fitted to an appropriate equivalent circuit model based on the shape and number of semi-circles detected in the Nyquist plot. Optical absorption/transmission spectra is analyzed using spectral fitting tools previously developed for analysis of QCM conductance spectra (Figure 4). Intensity of excitation light, measured wavelength range, and integration time can be controlled autonomously using feedback from previously measured optical spectra. The resulting system is a fully-autonomous scalable multifunctional film characterization tool with native capabilities for in situ data analytics and modeling.

To reduce computational strain on the experimental control system, storage and processing of experimental data are offloaded from the local PC to the ORNL Compute and Data Environment for Science (CADES) remote server in real-time. The IMES control software transfers experimental data and runs data processing scripts on CADES using secure shell (SSH) networking. The analysis results are sent back to the local machine, where they are used as feedback for the experiment parameters. Direct linking of CADES to the IMES control software highlights the benefits of remote cloud use for data management. Cloud resources also enable potential development of a network of scalable laboratory systems in which a single virtual machine remotely operates concurrent experiments in multiple laboratories. Future systems may consist of collaborative experiments running in different locations around the world which may be controlled and viewed in real-time by any human operator with access to the network.

The next several chapters describe specific materials characterization experiments that were carried out using the IMES system, software, and associated workflow.

Personal contributions

As modern science is inherently collaborative, the studies described in the following chapters represent the efforts of many different researchers. Therefore it is worth identifying my personal contributions to the work. I was the primary researcher responsible for building the IMES experimental setup, including integration of vacuum chamber feedthroughs, gas/vapor flow control system, and auxiliary electronics. I prepared many of the samples by spin-coating or drop-casting. I was the sole designer and developer of the experimental control software which was written in both LabVIEW and Python. I prepared, performed, and analyzed all electrical measurements, including DC and AC measurements. I prepared, performed, and analyzed all gravimetric and viscoelastic measurements acquired using the QCM. I was the primary developer of the software used for analyzing and modeling QCM data. I participated in interpretation of all experimental results and contributed to the writing of all manuscripts included in this work. In the following chapters that contain studies which were previously published, only the experimental techniques and analysis which were performed primarily by me are included. The full studies are referenced at the beginning of each chapter.

Chapter 3: Oxygen and humidity response of CuPc

A version of this chapter was originally published By Eric Muckley, Nicholas Miller, Christopher Jacobs, Thomas Gredig, and Ilia Ivanov:

Muckley, E.S., Miller, N., Jacobs, C.B., Gredig, T. and Ivanov, I.N., 2016. Morphology-defined interaction of copper phthalocyanine with O₂/H₂O. *Journal of Photonics for Energy*, 6(4), p.045501.

The copper phthalocyanine thin films were deposited by Nicholas Miller. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Abstract

Copper phthalocyanine (CuPc) is an important hole transport layer for organic photovoltaics (OPVs), but interaction with ambient gas/vapor may lead to changes in its electronic properties and limit OPV device lifetimes. CuPc films of thickness 25 nm and 100 nm were grown by thermal sublimation at 25°C, 150°C, and 250°C in order to vary morphology. We measured electrical resistance and film mass in situ during exposure to controlled pulses of O₂ and H₂O vapor. CuPc films deposited at 250°C showed a factor of 5 higher uptake of O₂ as detected by a quartz crystal microbalance (QCM), possibly due to formation of β-CuPc at T > 200°C which allows higher O₂ mobility between stacked molecules. While weight-based measurements stabilize after ~10 minutes of gas exposure, resistance response stabilizes over times > 1 hour, suggesting that mass change occurs by rapid adsorption at active surface sites whereas resistive response is dominated by slow diffusion of adsorbates into the bulk film. The 25 nm films exhibit higher resistive response than 100 nm films after an hour of O₂/H₂O exposure due to fast analyte diffusion down to the film/electrode interface. We found evidence of

decoupling of CuPc from the gold-coated QCM crystal due to preferential adsorption of O₂/H₂O molecules on gold.

Introduction

The emergence of organic electronics highlights the importance of low-cost functional materials for flexible thin film applications⁷³. Copper phthalocyanine (CuPc) is an aromatic macrocycle being explored for use in organic photovoltaics (OPVs)⁷⁴, organic light-emitting diodes (OLEDs)⁷⁵, organic field effect transistors (OFETs)⁷⁶, biosensors⁷⁷, and gas sensors⁷⁸. Its p-type behavior, strong optical absorption in the UV-vis wavelength range, and low cost due to industrial-scale production (> 60,000 tons annually⁷⁹) as a blue pigment for inks, plastics, and textiles makes CuPc well-suited for applications in low cost flexible devices⁸⁰⁻⁸¹.

Although CuPc is thermally and chemically stable under ambient conditions⁸², adsorption of gas molecules can facilitate charge transfer which alters the intrinsic electronic properties of CuPc films⁸³, leading to significant performance losses in OPVs. Electronic conductivity of metal phthalocyanines arises primarily from doping by electron-accepting O₂ and H₂O, which increases hole density and perturbs surface potential by addition of negatively-charged adsorbate molecule to the film surface⁸⁴⁻⁸⁵. Oxygen coordination occurs at the central metal atom⁸⁶ while H₂O sorption is generally attributed to hydrogen bonding near crystal domain boundaries⁸⁷⁻⁸⁸. Exposure to higher H₂O partial pressure leads to the formation of H₂O multi-layers on CuPc domain surfaces, resulting in switching from electronic to ionic conduction, which further increases conductivity⁸⁹⁻⁹⁰. Moreover, O₂/H₂O adsorption may facilitate fracture, displacement, and rearrangement of CuPc domains by disturbing intermolecular and molecule-substrate adhesion⁹¹.

The response of metal phthalocyanines to organic vapors and noxious gases has been well-characterized^{88, 91-92}. It is recognized that CuPc film morphology and layer thickness play an important role in electronic properties and gas response of CuPc films, but the relationship between morphology, mass loading by analyte molecules such as H₂O/O₂, and the electrical response of CuPc has not been thoroughly investigated⁹³⁻⁹⁵. During thermal deposition of CuPc, molecules align by weak van der Waals and π - π interactions, resulting in electron delocalization along the Cu atom stacking axis⁸¹⁻⁸². Substrate heating enhances mobility of deposited molecules, allowing formation of longer molecular chains which further self-assemble to form elongated crystallites. Crystalline domain growth is often associated with changes in film porosity and roughness^{89, 96}. Faster gas response can be achieved for higher film porosity due to increased surface area^{87, 97}. Surface area and number of inter-grain boundaries which impede charge transport typically decrease as domains grow larger⁹⁸. Since response time is primarily related to slow diffusion of adsorbates into the film bulk⁸³, the response time is inversely proportional to film thickness, since surface area to volume ratio decreases as thickness increases⁸². In thinner films charge transport layers lie closer to the film/gas interface and therefore the effects of adsorption-induced surface trap states are enhanced⁹². An understanding of the influence of film morphology on CuPc gas response is critical for extending device lifetimes and improving gas sensor performance.

Here we study the CuPc gas/vapor response by measuring changes in electrical resistance and mass of films exposed to O₂ and H₂O. This allows us to directly observe the relationship between gas sorption/desorption kinetics and the electrical response of the same film to gas/vapor exposure.

Experiment

Purified CuPc was purchased from Sigma Aldrich and used without purification. CuPc films were deposited by thermal sublimation onto pre-cleaned platinum interdigitated electrodes and gold-plated 5 MHz AT-cut quartz crystal microbalance (QCM) crystals. Film deposition was carried out in a thermal evaporator (Nanomaster NTE-3000). During thermal evaporation, substrates were held at 25°C, 150°C, and 250°C. Film thickness was monitored in situ using a QCM system to produce both 25 nm and 100 nm thick films at each deposition temperature.

Prior to gas/vapor sorption measurements, films were placed under 10^{-6} Torr (1.33×10^{-6} mbar) vacuum for 3 hours. QCM frequency change was recorded using an SRS QCM200 and electrical resistance was recorded using a Keithley 6430 source-meter with preamplifier. Pulses of O₂ and H₂O vapor with pressures 5, 10, 15, and 20 Torr were injected into the vacuum chamber using two mass flow controllers. A LabVIEW program was used to control the gas/vapor flow and record resistivity and QCM frequency shift during the experiment. All measurements were performed at $27 \pm 0.5^\circ\text{C}$ using a modified pressure/flow control system from Surface Measurement Systems. Frequency shift of the QCM crystals during the experiment was converted to mass change using the Sauerbrey equation³⁶.

To confirm that morphology of the CuPc films changed with deposition temperature, atomic force microscope (AFM) images of each film were acquired using a NTEGRA Spectra microscope (NT-MDT). The AFM was operated in semi-contact (tapping) mode at 73 kHz tip resonance frequency with a 0.7 Hz line scan rate.

Results and discussion

AFM images of 25 nm (top row) and 100 nm thick (bottom row) CuPc films deposited at 25°C, 150°C, and 250°C are shown in Figure 5. Film morphology is consistent with temperature-induced grain size growth observed in previous studies on CuPc films⁹⁸. Increasing deposition temperature results in larger elongated domains due to increased molecular diffusion leading to the formation of a longer molecular stacking along the axis of the central Cu atom. The 100 nm films generally contain larger domains than the 25 nm CuPc films. In all cases except for the 25 nm film deposited at 150°C, film roughness increases with the deposition temperature. While short-range roughness ($r < x_i$, where x_i is the correlation length or size of the grain) decreases at higher deposition temperatures due to flattening of the domains, long-range roughness ($r > x_i$) increases with temperature, likely due to the presence of structural imperfections like pinholes which increase film porosity at higher temperatures. Such structural imperfections are speculated to arise due to Ehrlich-Schwoebel-like energy barriers which break the domain growth symmetry⁹⁹. Resistance response (R/R_0) and mass change (ΔM) of CuPc films exposed to different pressures of H₂O and O₂ are shown in Figure 6 during 4-pulse sequences of H₂O and O₂ (shown in bottom panel). Resistance of CuPc decreases in response to both H₂O and O₂, indicating that both analytes behave as electron acceptors. H₂O/O₂ sorption leads to charge transfer which increases hole density, resulting in higher conductivity, in agreement with previous studies⁸⁴⁻⁸⁵. In films deposited at temperatures over 25°C, resistance change occurs over long timescales (> 1 hour), even during isobaric conditions. Thus, not all films reach an equilibrated steady-state condition before the next gas pulse begins. During the 5 Torr H₂O pulse, R/R_0 and ΔM kinetics are qualitatively like those of the next pulses. This suggests that blocking of active adsorption sites results in surface activity, which is like that of pristine surfaces, even though some sites are occupied. Since the

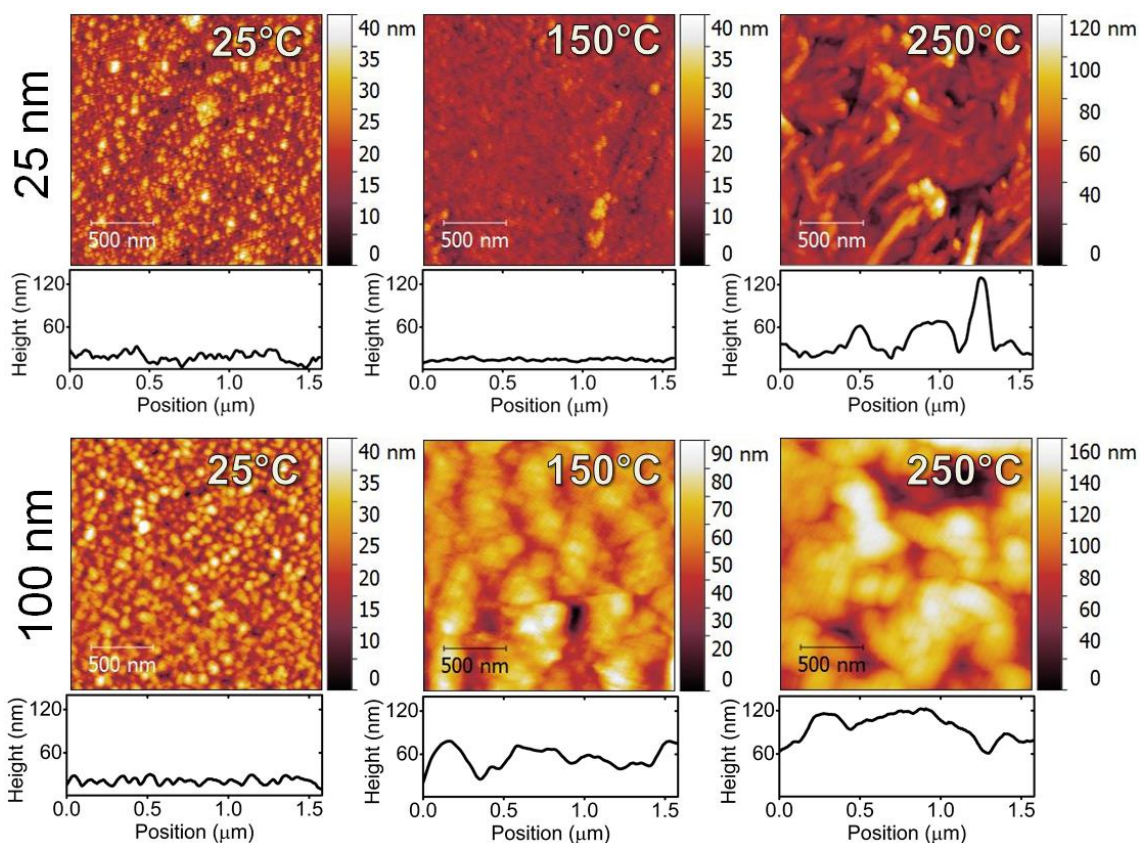


Figure 5. AFM images of 25 nm thick and 100 nm thick (top and bottom rows, respectively) CuPc films deposited on glass substrates at 25°C, 150°C, and 250°C. Line profiles correspond to the bottom row of pixels in each image. Figure reproduced with permission.⁵⁷

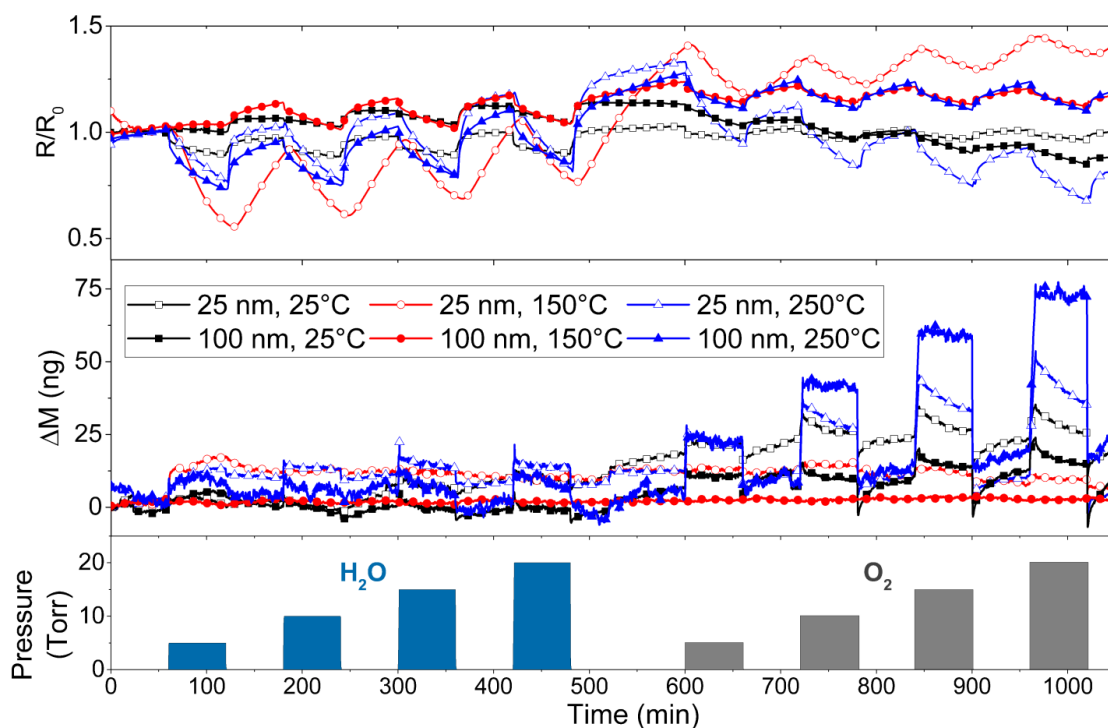


Figure 6. Resistance response (R/R_0 , top panel) and mass change (ΔM , middle panel) of CuPc films during exposure to different pressures (bottom panel) of H_2O vapor (blue colored pulses) and O_2 (gray colored pulses). Films are labeled by their thickness (25 or 100 nm) and the temperature of the substrate during deposition (25°C, 150°C, or 250°C), with a generic name of XX nm, YY°C. Figure reproduced with permission.⁵⁷

focus of this experiment is to study the effect of morphology on gas response, and each film is exposed to the same sequence of gas pulses, the gas/vapor responses were used to compare between different films without reaching equilibrium.

As shown in the central panel of Figure 6, mass loading of films changes most appreciably during O₂ exposure and is proportional to O₂ pressure. The response dynamics were further examined using background-corrected resistance ($R/R_0=1$) and mass normalized to $\Delta M=0$ just before exposure to the 20 Torr H₂O/O₂ pulses. The results are summarized in Figure 7(a) and Figure 7(b) for H₂O and O₂ response of the CuPc films. Vertical dashed lines in Figure 7(a) and Figure 7(b) identify the beginning and end of gas/vapor exposure. Corresponding changes in mass during the gas/vapor exposure are shown in Figure 7(c) and Figure 7(d). Upon initial exposure to H₂O/O₂, rapid mass loading occurs, primarily in films deposited at 250°C. The change in mass ΔM is larger for 100 nm films than 25 nm films, which is expected since thicker films provide more active adsorption sites than the thinner films. Film recovery (desorption of H₂O/O₂) occurs over less than 5 minutes after exposure of films to vacuum. Mass change in the CuPc appears almost instantaneous and completely reversible. In contrast, changes in resistance of CuPc occur over much longer time scales (> 1 hour) and are not completely reversible, especially for O₂ desorption. The difference in R/R_0 and ΔM response times suggest that different mechanisms are responsible for resistance and mass changes of CuPc films. Mass loading of CuPc films and at domain boundaries occurs rapidly but does not significantly alter charge carrier density near the charge transport layers (located at the film-substrate interface). Since films were deposited on substrates with pre-patterned electrodes, it is likely that only charge carriers in domains near the film-substrate interface contribute to the resistive gas/vapor resistance. Only after adsorbates diffuse deep enough into the bulk film to reach charge transport regions near the CuPc-electrode interface, which occurs on the order of hours, does the conductivity increase.

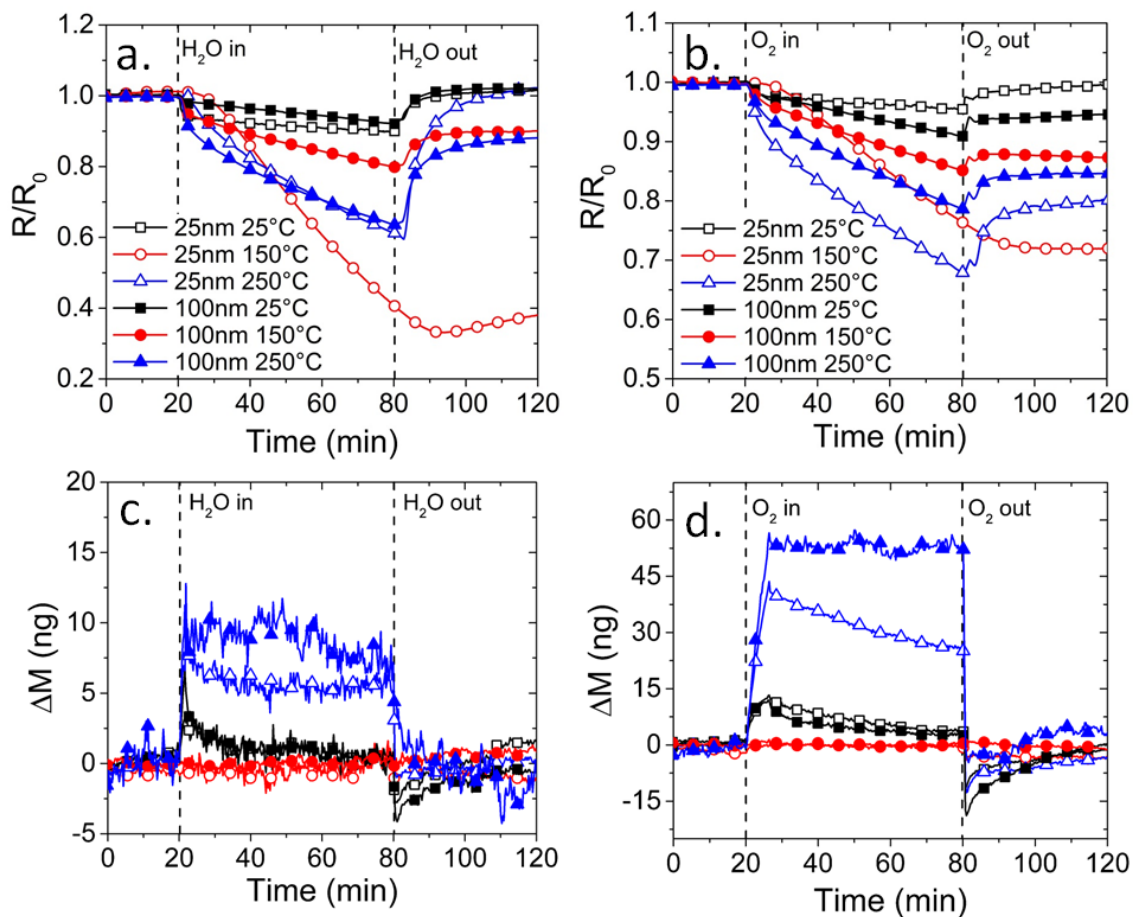


Figure 7. Normalized resistance change (R/R_0) during exposure to 20 Torr pulses of H₂O vapor (a) and O₂ (b) for 1 hour. Normalized mass change (ΔM) in response to exposure of CuPc films to 20 Torr H₂O vapor (c) and O₂ (d) for 1 hour. Figure reproduced with permission.⁵⁷

Kerp et al. reported that mass loading saturation of micron-thick zinc phthalocyanine films by O₂ adsorption occurs on a timescale of minutes⁹⁰. That data reported here suggest that the saturation reported by Kerp is a consequence of adsorbate crowding at surface adsorption sites, not saturation of the bulk film by O₂, which occurs over hours. The slow diffusion of adsorbates toward the film-electrode interface observed here is consistent with the findings of Passard et al. who found that gas response occurred over timescales > 1 hour in 300 nm polyfluoro-aluminum phthalocyanine films⁸³.

It should be noted that the 25 nm film deposited at 150°C exhibits the highest resistive H₂O response and the slowest response kinetics. The initial resistive response does not take place until after 5 minutes after the gas/vapor pressure in the measurement chamber has changed. This is likely related to the morphology of the film, as shown in Figure 5. The 25 nm film deposited at 150°C exhibits the lowest roughness of any other film in the series, which suggests a high density and low film porosity. The low porosity leads to slow adsorbate diffusion in and out of the film, resulting in slower response kinetics and poor reversibility. This film also appears to have a lower average thickness than the other films and subsequently a higher eventual resistive response.

Figure 8 shows magnitude of the resistance change (ΔR) of each film after 1-hour exposure to 20 Torr pulses of H₂O vapor (a) and O₂ (b). The ΔR response to both H₂O and O₂ generally increases with film deposition temperature. This is likely due to increases in film porosity which result from the growth of larger domains. The porosity improves access to active adsorption sites by facilitating adsorbate diffusion through open channels, increasing the rate at which adsorbates reach charge transport layers near the film/electrode interface. ΔR is generally higher for 25 nm films than 100 nm films since adsorbate migration to electrodes occurs more rapidly. This finding agrees with the results of others who

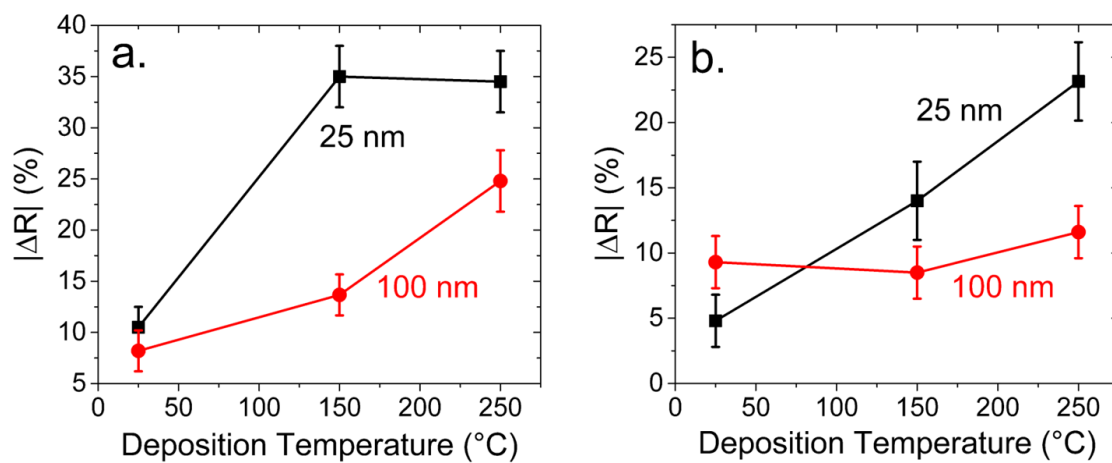


Figure 8. The resistance change ($|\Delta R|$) of 25 nm and 100 nm thick films during 1-hour exposure to 20 Torr pulses of H_2O vapor (a) and O_2 (b) as a function of film deposition temperature. Figure reproduced with permission.⁵⁷

show that film thickness is directly related to the magnitude and response time of the resistive CuPc gas/vapor response^{83, 97}.

Mass changes in films during 20 Torr gas/vapor pulses are shown in Figure 9(a). As mentioned previously, mass loading occurs most significantly in films deposited at 250°C. Mass loading of O₂ is enhanced by over a factor of 5 in β -phase CuPc films deposited at 250°C. At roughly 200°C, CuPc undergoes a meta-stable triclinic α -phase to stable monoclinic β -phase transition characterized by an increase in the tilting angle between the molecular and stacking axes, resulting in less π - π overlap between adjacent molecules⁸². The transition increases spacing between the central metal atoms of adjacent stacked molecules from roughly 3.8 Å to 5 Å¹⁰⁰. Since the van der Waals radius of O₂ is approximately 1.5 Å¹⁰¹, extra space between β -phase stacked molecules may allow greater O₂ mobility toward central Cu atoms, so the formation of β -phase domains may significantly enhance O₂ coordination and increase the amount of physisorbed O₂ in CuPc films deposited at 250°C⁸⁶. The CuPc $\alpha \rightarrow \beta$ transition is also associated with an increase in film roughness¹⁰² which leads to higher surface area and an increase in the number of accessible adsorption sites. This effect may be responsible for the slight increase in H₂O loading of films deposited at 250°C. Since H₂O adsorption occurs primarily around grain boundaries⁸⁷⁻⁸⁸, it is expected that the $\alpha \rightarrow \beta$ transition has less of an effect on H₂O loading than on O₂ loading. The 100 nm thick films exhibit higher ΔM than 25 nm thick films because they necessarily contain more adsorption sites and thus allow accommodation of more adsorbate molecules.

It is informative to examine the behavior of ΔM during H₂O/O₂ exposure. The average time derivative of film mass (dM/dt) was extracted from ΔM curves shown in Figure 6 during H₂O/O₂ exposure. dM/dt values were averaged over isobaric conditions (highlighted in green in the inset of Figure 9(a)). Continuous H₂O/O₂ loading of rigid films would result in a positive value for the derivative

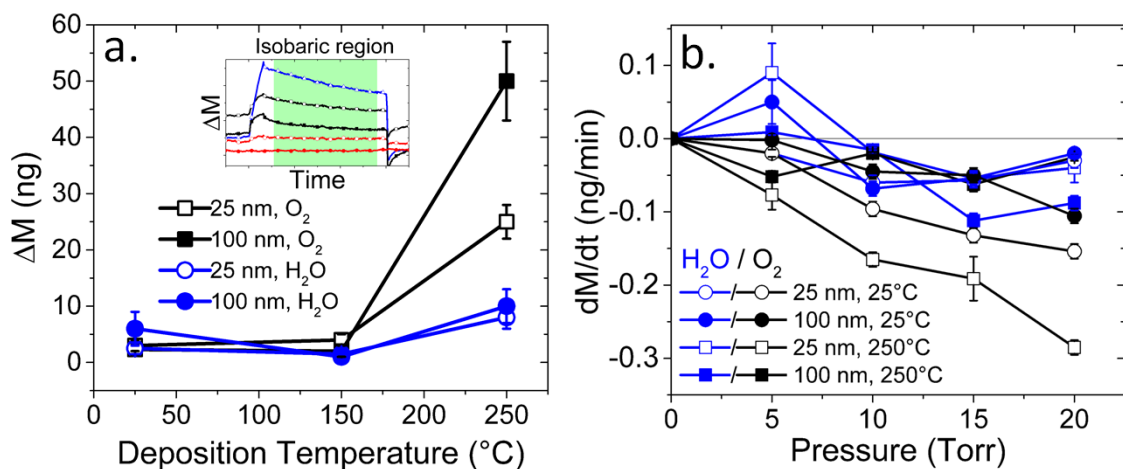


Figure 9. (a) Total mass change (ΔM) in response to 20 Torr pulses of O_2 (black) and H_2O (blue), shown for 25 nm and 100 nm thick films deposited at 25 $^{\circ}\text{C}$, 150 $^{\circ}\text{C}$, and 250 $^{\circ}\text{C}$. The inset is related to Figure 9(b). (b) Average time derivative of film mass (dM/dt) during O_2 exposure (black) and H_2O exposure (blue) after initial rapid mass loading has occurred. dM/dt is extracted during $\text{O}_2/\text{H}_2\text{O}$ exposure under isobaric conditions, highlighted in green in the inset of (a). For clarity, data from films deposited at 150 $^{\circ}\text{C}$ are not shown since $dM/dt \approx 0$ g/s. Figure reproduced with permission.⁵⁷

($dM/dt > 0$) during the entire length of the gas/vapor pulse. However, after an initial mass increase which occurs on a time scale of ~ 5 minutes, we observe that the sign of the derivative changes ($dM/dt < 0$), in all films except for during the 5 Torr H_2O pulses. Since it is unlikely that significant desorption of adsorbates occurs during isobaric conditions, we propose that sorption-induced changes in mechano-structural and/or viscoelastic properties of the films are responsible for the apparent decreases in mass. Voinova et al. showed that materials undergoing changes in viscoelasticity may display signatures of mass loss during QCM measurements¹⁰³. The Sauerbrey equation, which is strictly valid only for thin uniform films which are rigidly bound to the quartz oscillator is no longer valid³⁶. The apparent loss of mass has also been observed in other organic films undergoing adsorption of H_2O and O_2 on QCM crystals⁵⁸. Since H_2O sorption generally occurs by hydrogen bonding near grain boundaries⁸⁷⁻⁸⁸ and can result in the formation of an H_2O meniscus on the CuPc surface⁸⁹⁻⁹⁰, it is likely that high H_2O pressures leads to formation of H_2O multilayer structures near inter-grain interfaces. This increases the probability of slippage between adjacent grains as they oscillate at the 5 MHz fundamental frequency of the QCM. Inter-grain and CuPc-gold slip motion increase the resonant frequency of the oscillator, which results in the apparent decrease in film mass. Ojifinni et al. reported that H_2O adsorption on gold surfaces may result in formation of H_2O -Au, H_2O -O, or OH complexes in the presence of oxygen adatoms¹⁰⁴. Moreover, evidence of CuPc molecule detachment/rearrangement on gold substrates due to preferential O_2/H_2O adsorption has been reported⁹¹. Both of these processes represent possible pathways for decoupling of rigid CuPc-gold interactions which increases f_0 as CuPc molecules are effectively lifted off the QCM surface or their network is disrupted. The positive value of dM/dt during H_2O loading at 5 Torr provides evidence that the limited water adsorption at this pressure does not induce significant mechano-structural changes in the films.

The mass rate dM/dt exhibits higher pressure dependence during O_2 loading than during H_2O loading. O_2 coordination with central Cu atoms⁸⁶ may disrupt π - π stacking and lead to domain fracture and rearrangement of CuPc⁹¹.

Preferential adsorption of O_2 on gold may be responsible for displacing CuPc from the QCM surface, leading to an increase in f_0 . The O_2 -induced decrease in mass is most evident in 25 nm thick films, which show a roughly linear decrease in the value of the derivative dM/dt with O_2 pressure. Slow diffusion of O_2 through the CuPc⁸³ to the QCM surface must occur before disruption of CuPc-gold adhesion takes place, so it is reasonable that dM/dt observed in 25 nm films is more pronounced than in 100 nm films. The pressure dependence of dM/dt is a result of faster diffusion of O_2 into the bulk film and to the film-crystal interface when more adsorbate molecules are present.

Conclusions

We investigated separately effects of film morphology and thickness on the interaction of H_2O and O_2 with CuPc. By measuring electrical resistance of films and frequency shift of CuPc-coated QCM crystals, we studied the relation between sorption/desorption kinetics and film conductivity. While mass loading occurred relatively quickly after gas/vapor exposure (< 10 minutes), resistance changes occurred over much longer time scales (> 1 hour). This suggests that the resistive CuPc gas/vapor response is dominated by slow diffusion of adsorbates into the film bulk, while mass change occurs by rapid adsorption at active surface sites. Resistive response to analyte gas/vapor generally increases with film deposition temperature due to increased porosity stemming from larger crystal domains. 25 nm thick films exhibit higher resistive response than 100 nm thick films due to the smaller analyte diffusion length required for reaching the film/electrode interface. O_2 loading of films was enhanced by a factor of 5 in films deposited at 250°C. We suggest that this may be a consequence of the CuPc

$\alpha \rightarrow \beta$ phase transition which occurs around 200°C and results in higher O₂ mobility between stacked molecules, facilitating O₂ coordination at the central Cu atoms. Finally, we found evidence of H₂O/O₂-induced mechano-structural changes in the films. This is likely due to slipping motion between CuPc crystallites, and between CuPc and the Au electrode of the QCM oscillator. We propose that mechanical decoupling of CuPc from the gold-coated QCM crystal is caused by preferential adsorption of H₂O/O₂ molecules on gold.

Chapter 4: Humidity response of water-soluble CuPc

A version of this chapter was originally published by Eric Muckley, Christopher Jacobs, Keith Vidal, Nickolay Lavrik, Bobby Sumpter, and Ilia N. Ivanov:

Muckley, E.S., Jacobs, C.B., Vidal, K., Lavrik, N.V., Sumpter, B.G. and Ivanov, I.N., 2017. Multi-mode humidity sensing with water-soluble copper phthalocyanine for increased sensitivity and dynamic range. *Scientific reports*, 7(1), p.9921.

Spectroscopic ellipsometry was performed by Keith Vidal and Christopher Jacobs. Interdigitated electrodes were fabricated by Nickolay Lavrik. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Abstract

Aqueous solubility of copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (CuPcTs) enables fabrication of flexible electronic devices by low cost inkjet printing. We (1) investigate water adsorption kinetics on CuPcTs for better understanding the effects of relative humidity (RH) on hydrophilic phthalocyanines, and (2) assess CuPcTs as a humidity-sensing material. Reaction models show that H₂O undergoes 2-site adsorption which can be represented by a pair of sequentially-occurring pseudo-first order reactions. Using high frequency (300-700 THz) and low frequency (1-8 MHz) dielectric spectroscopy combined with gravimetric measurements and principal component analysis, we observe that significant opto-electrical changes in CuPcTs occur at RH $\approx$ 60%. The results suggest that rapid H₂O adsorption takes place at hydrophilic sulfonyl/salt groups on domain surfaces at low RH, while slow adsorption and diffusion of H₂O into CuPcTs crystallites leads to a mixed CuPcTs-H₂O phase at RH > 60%, resulting in high frequency dielectric screening

of the film by water and dissociation of Na^+ from $\text{CuPc}(\text{SO}_3^-)_4$ ions. The $\text{CuPcTs-H}_2\text{O}$ interaction can be tracked using a combination of gravimetric, optical, and electrical sensing modes, enabling accurate ($\pm 2.5\%$) sensing in the $\sim 0\text{-}95\%$ RH range with a detection limit of less than 0.1% RH.

Introduction

Metal phthalocyanines (MPcs) comprise a family of semiconducting aromatic macrocycles found in a broad range of optoelectronic devices and sensors^{25, 105}. Although MPcs are well-suited for use in lightweight flexible devices, films are typically grown by vacuum thermal evaporation. Modification of the aromatic moiety with four sulfonic groups allows solubility of MPcs in water and other solvents, which greatly simplifies their deposition for catalysis¹⁰⁶, photodynamic therapy¹⁰⁷, photovoltaics (OPVs)¹⁰⁸, and liquid crystal displays (LCDs)¹⁰⁹. Of particular interest among sulfonated MPcs is copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (CuPcTs) because of its p-type behavior, gas sensing properties, high solubility, and large-scale production as an industrial pigment¹¹⁰⁻¹¹¹. Despite the hydrophilic character of sulfonyl/salt complexes, the response of sulfonated MPcs like CuPcTs under changing relative humidity (RH) conditions has not been thoroughly studied¹¹²⁻¹¹³. Both electronic and ionic mobility in CuPcTs film can be altered by uptake of water^{57, 114}. The presence of H_2O at SO_3Na groups induces salt dissociation, leading to formation of Na^+ and $\text{CuPc}(\text{SO}_3^-)_4$ ions¹¹⁵⁻¹¹⁶ which contribute to charge transport in CuPcTs at $\text{RH} > 45\%$ ¹¹³. Although water-induced conductivity changes are fully reversible after film dehydration, ionic dissociation and H_2O multi-layer formation at high RH conditions can result in creation of a mechanically-unstable MPc- H_2O pseudo-solution mixed phase¹¹⁶⁻¹¹⁷, allowing CuPcSO_3 migration along the substrate surface due to interaction with H_2O layers. Mobility of $\text{CuPc}(\text{SO}_3^-)_4$ ions

can result in morphological changes including domain displacement and fracture^{91, 112}.

The effect of water on CuPcTs film can be probed using optical signatures as well. While optical response of sulfonated phthalocyanines has been well-studied in solution, less information is available about water interaction with solid films^{115, 118}. The electronic absorption spectrum of CuPc has two prominent features which arise from $\pi \rightarrow \pi^*$ transitions: the Q band (~600-750 nm), associated with a_{1u} to e_g^* orbital transitions, and the B (Soret) band (~300-450 nm), associated with a_{2u} to e_g^* orbital transitions¹¹⁹⁻¹²⁰. In crystals with unit cells composed of n molecules, the nondegenerate excited states of each molecule are comprised of n bands, resulting in several absorption peaks¹²¹. This is the so-called Davydov splitting observed in all MPcs which gives rise to the Q_A , Q_B and Q_{CT} sub-bands¹²². Changes in the optical spectra are related to specific electronic transitions which reveal the effect of water on charge transfer (Q_{CT}), excitonic transitions (Q_A , and Q_B), and bandgap energy. While Ghani et al. investigated solvatochromic properties of MPcs exposed to a series of organic solvents¹²⁰, systematic efforts to relate H₂O adsorption to changes in optoelectronic properties of CuPcTs have not been undertaken, despite findings by Aziz et al. that MPcs functionalized for solution processing show promise for RH sensing applications¹²³.

Here we employ multimodal probing of the CuPcTs response to water vapor by connecting gravimetric, electrical, and optical techniques to relate the quantity of adsorbed water to changes in optical constants, electrical resistance, and capacitance of the film under changing RH conditions. We use several isotherm models to examine the kinetics of water adsorption, which reveals a complex adsorption mechanism that involves at least two different adsorption sites, including a dominant process which is active in the entire measurement range (~0-95% RH) and one which becomes active for RH > 60%. Combining

gravimetric and optical techniques, we demonstrate the possibility of humidity sensing in the 0-95% RH range with $\pm 2.5\%$ resolution.

Experiment

Copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (dye content 85%, in water) was purchased from Sigma Aldrich and used without further purification. CuPcTs films were deposited from solution on pre-cleaned 5 MHz AT-cut gold-coated quartz crystal microbalance (QCM) crystals with 1 cm² active electrode area, conductive n-doped SiO₂ substrates, and undoped SiO₂ substrates with pre-patterned gold interdigitated electrodes (10 nm thickness, 2 μ m spacing, 100 digits per electrode). Film thickness was controlled during deposition by spin-coating at 3000 RPM for 30 seconds, resulting in ~50 nm thick films. Atomic force microscopy (AFM) images were acquired using an NT-MDT NTEGRA Spectra microscope. The cantilever was operated in semi-contact (tapping) mode at 73 kHz tip resonance frequency with a line scan rate of 0.7 Hz.

Prior to H₂O adsorption measurements, films were placed under 10⁻³ Torr (1.33 $\times$ 10⁻³ mbar) vacuum for 24 hours. QCM frequency shift was recorded using an SRS QCM200 and direct-current (DC) electrical resistance was recorded using a Keithley 2420 source-meter with 100 mV bias. Frequency shift of the QCM crystals was converted to mass change using the well-known Sauerbrey equation³⁶. Electrochemical impedance spectroscopy (EIS) was performed using a Zahner IM6 electrochemical workstation. Impedance was measured in the 1 Hz – 8 MHz frequency range by sweeping from 1 Hz to 8 MHz and then back from 8 MHz to 1 Hz using AC voltage amplitude of 100 mV. RH conditions were controlled by injecting water vapor into the vacuum chamber using a mass flow controller at 20 cm³/min flow rate. The humidity level was measured by continuous monitoring of the pressure of the H₂O vapor inside the vacuum

chamber. Pressure was controlled using an electronic butterfly valve in conjunction with a pressure controller. A LabVIEW program was used to control the H₂O flow and record resistivity of the film and frequency shift of the QCM during the experiment. All measurements were performed at $27 \pm 0.5^\circ\text{C}$ inside a modified controlled environmental chamber from Surface Measurement Systems.

Spectroscopic ellipsometry (SPE) measurements were obtained at 1.5 nm steps from 275-1000 nm at 75° incident angle using a J.A. Woollam Co. M-2000 ellipsometer. A flow cell with optical windows was used to control the sample environment during SPE measurements. RH levels inside the flow cell were controlled using an L&C Science RH-200 humidity generator and measured with an additional humidity probe at the outlet of the flow cell. Before initiating SPE measurements, the CuPcTs film was exposed to 3% RH for 3 hours. For modeling SPE data, the CuPcTs layer was represented by a single isotropic layer consisting of five Lorentz oscillators¹²⁴. A Levenberg–Marquardt algorithm was used for fitting oscillator parameters. The fitted region was reduced to the 450-900 nm range to reduce the standard error.

Results and discussion

Film morphology

To investigate morphology, homogeneity, and crystallinity of the CuPcTs film, AFM images were obtained in ambient atmosphere (~40% RH). The CuPcTs film consists of elongated grains up to 600 nm long and 250 nm wide with RMS roughness of 6 nm over a 5 μm length (Figure 10(a)). As calculated from SPE measurements, the optical film thickness was roughly 50 nm when measured at ambient RH. The average height visible in the AFM image is ~21 nm, which

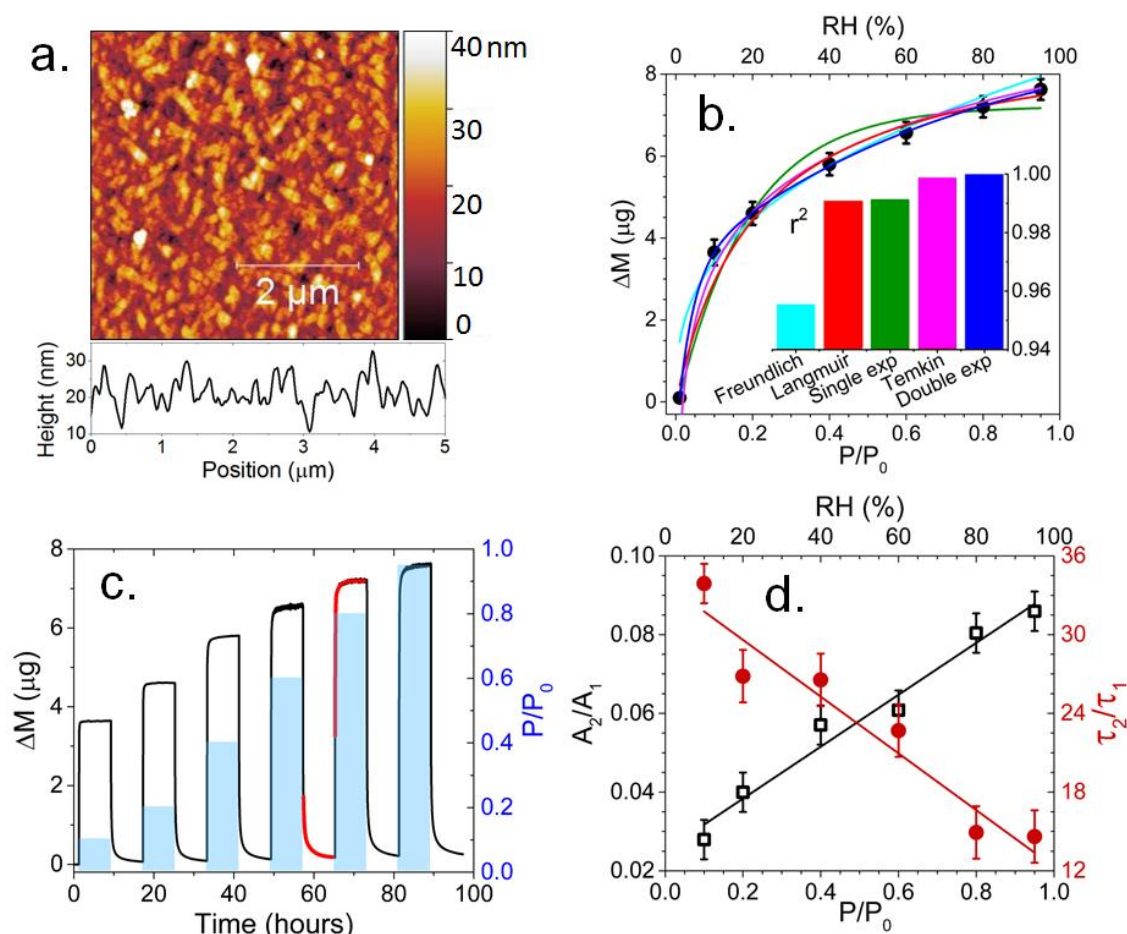


Figure 10. (a) AFM image of CuPcTs film. Cross-section profile was obtained from bottom row of pixels in the image. (b) H₂O adsorption isotherm (black circles) fit with five different isotherm models. The r^2 values of each fit are shown in the inset bar graph. Fit lines correspond to colors used in the bar graph. Error bars correspond to noise in the measured QCM signal. (c) Mass change (ΔM) (black, left axis) of CuPcTs film during exposure to pulses of H₂O vapor (blue, right axis). Red lines indicate examples of double exponential fits. (d) Ratio of double exponential fit parameters A_2/A_1 (black squares, left axis) and τ_2/τ_1 (red circles, right axis). Lines show linear fits. Error bars are propagated double exponential fitting errors. Figure reproduced with permission⁵⁵.

suggests that pinholes visible in the image penetrate to a depth of at least half of the film thickness. The presence of pinholes and large (10-100 nm diameter) interstitial spaces between grains result in high film porosity and surface area which allows for rapid H₂O diffusion into the bulk film.

Gravimetric humidity response

To probe the kinetics H₂O adsorption on CuPcTs film, as well as quantify mass gain during exposure to different humidity conditions, mass change (ΔM) of the film was measured under different water vapor partial pressures. The H₂O adsorption isotherm on CuPcTs (black points) was fitted to Freundlich (cyan), Langmuir (red), single exponential (green), Temkin (magenta), and double exponential (blue) models¹²⁵ in Figure 10(b). Vapor pressure of H₂O is reported in terms of P/P_0 , where P is the partial pressure of H₂O and P_0 is the saturation vapor pressure (~32 mbar at 27°C, so that $P/P_0 = 1$ corresponds to 100% relative humidity). The inset bar graph displays r^2 values for each of the fits. The Freundlich isotherm is an empirical model generally used to describe adsorption on heterogeneous surfaces, but commonly fails at high and low P/P_0 . Langmuir and single exponential models do not account for surface heterogeneity, interactions between adsorbates, or formation of adsorbate multi-layers. Temkin and double exponential models achieve $r^2 > 0.998$ and best represent the measured H₂O adsorption isotherm. The Temkin model is particularly well-suited for predicting gas phase equilibrium with surfaces that contain a distribution of binding energies and explicitly accounts for adsorbate-adsorbate interactions by acknowledging that the heat of adsorption decreases linearly with adsorbate coverage¹²⁵⁻¹²⁶. Double exponential behavior is typically observed in sorbents which contain sites associated with two or more distinct energies¹²⁷⁻¹²⁸. High correlation between experimental data and the Temkin and double exponential models suggests that H₂O adsorption occurs at heterogeneous binding sites,

including sites on the CuPcTs molecule as well as previously adsorbed H₂O molecules. Results from modelling of adsorption kinetics (Figure 11) and principal component analysis (Figure 12) suggest that at least two distinct adsorption sites are active during H₂O loading of CuPcTs film. Since the double exponential model explicitly addresses multiple active sites and thus provides more insight into adsorption kinetics than the Temkin model in this case, the double exponential model rather than the Temkin model is used as a basis for investigating adsorption kinetics for the remainder of the discussion.

Figure 10(c) shows mass change (ΔM) of the CuPcTs film during adsorption and desorption of water at different H₂O vapor pressures (blue pulses). Adsorption of H₂O on the CuPcTs film is completely reversible after about 10 hours of 10^{-3} mbar vacuum exposure following each H₂O pulse. Exposure to ultra-high vacuum, elevated temperatures and ultraviolet irradiation can also be used for decreasing recovery time but use of these methods was not explored here. Kinetics of H₂O adsorption visibly change as P/P_0 increases; i.e. the rising edge of the mass change becomes more rounded at higher pressures. The ΔM kinetics during both adsorption and desorption of water closely follow double exponential behavior ($r^2 > 0.99$) in the 10-95% RH range, as shown by the red double exponential fits to ΔM in Figure 10(c). Exponential heterogeneous (multi-site) adsorption kinetic models are of the form $\Delta M = M_0 + \sum_{i=1}^n A_i e^{-t/\tau_i}$, where n is the number of active sites, A_i corresponds to the relative amount of mass adsorbed at *Site-i*, and τ_i is the inverse of the adsorption rate constant at *Site-i*. Double exponential fit parameters were extracted from each adsorption regime shown in Figure 10(c). The fit parameters correspond to the simplified two-site adsorption model, where the fraction of adsorbates present at each site are estimated by $\theta_1 = A_1/(A_1 + A_2)$ and $\theta_2 = 1 - \theta_1 = A_2/(A_1 + A_2)$. To examine relative activity of two absorption sites with RH, we used the ratio of pre-exponential factors (A_2/A_1) and time constant parameters (τ_2/τ_1) derived from

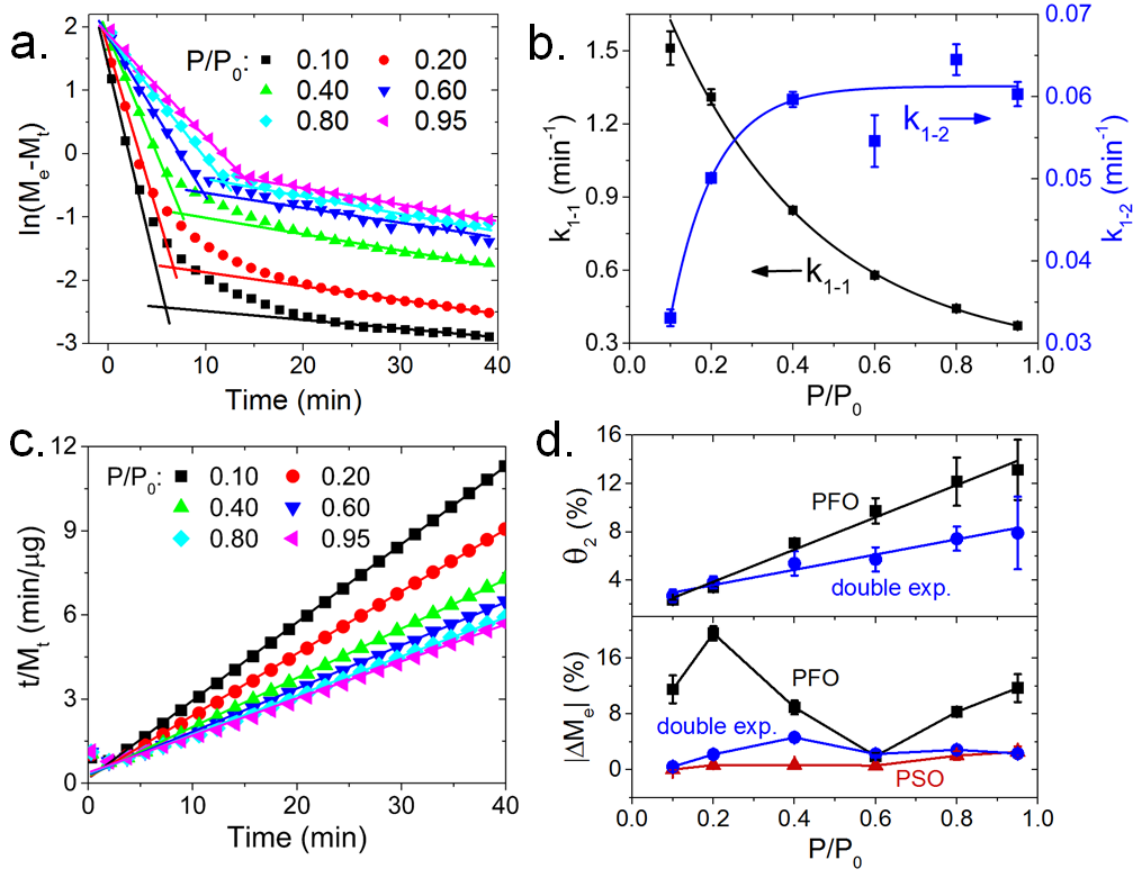


Figure 11. (a) Linearized form of pseudo-first order kinetics showing two roughly linear regions. (b) Reaction rate constants for first (k_{1-1}) and second (k_{1-2}) pseudo-first order kinetic processes identified in (a), shown with exponential fits. Error bars correspond to linear fitting errors. (c) Linearized form of the pseudo-second order kinetics showing highly linear behavior ($r^2 > 0.998$). (d) Top panel: comparison of *Site-2* occupancy (θ_2) as estimated from pseudo-first order kinetic and double exponential models. Bottom panel: percent difference ($|\Delta M_e|$) between measured equilibrium mass (M_e) and equilibrium mass predicted by pseudo-first order, pseudo-second order, and double exponential kinetic models. Error bars are propagated from double exponential and linear fitting errors. Figure reproduced with permission.⁵⁵

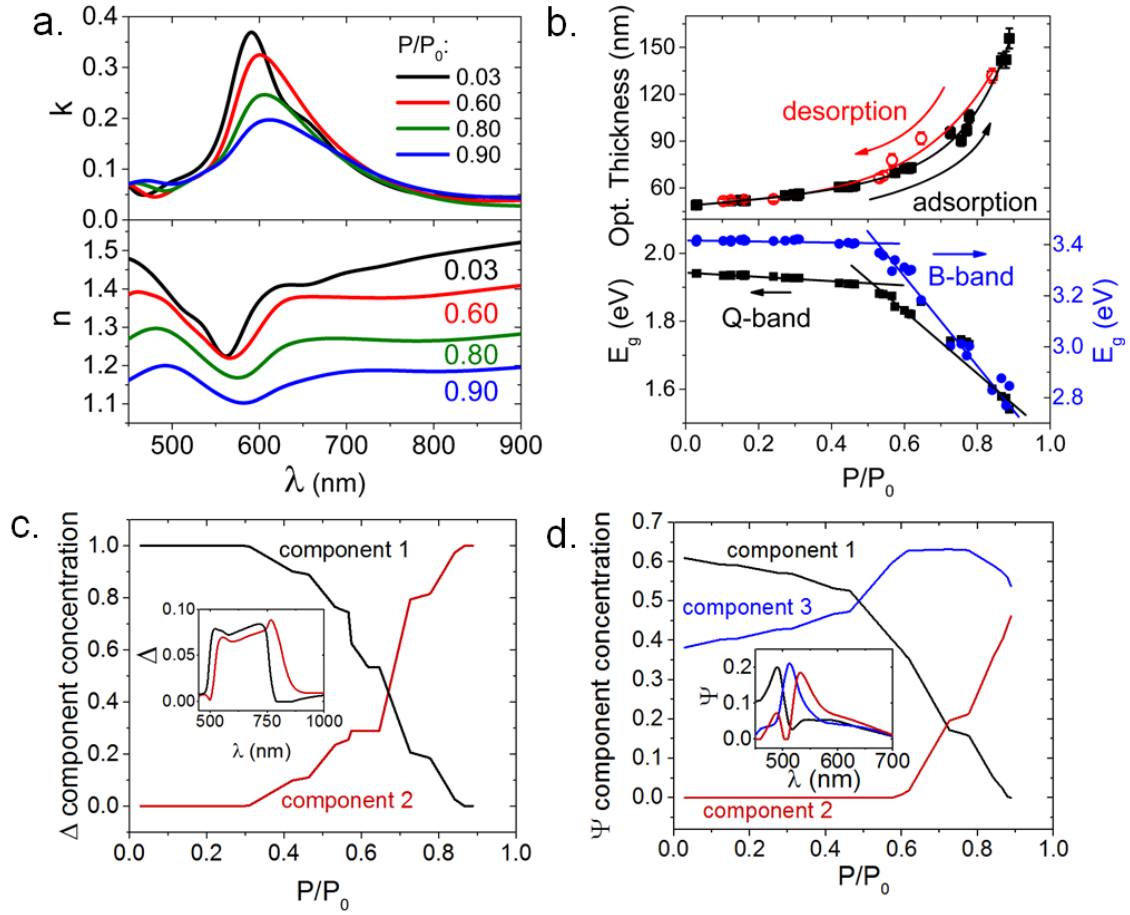


Figure 12. (a) Wavelength-dependent extinction coefficient (k) (top panel) and index of refraction (n) (bottom panel) of CuPcTs film under changing RH. (b) Top panel: Optical film thickness under increasing (adsorption, black squares) and decreasing (desorption, red circles) RH. Lines show exponential fits. Error bars correspond to errors propagated from fitting to the Lorentz oscillator model. Bottom panel: Bandgap energy (E_g) of Q-band (left axis) and B-band (right axis). Straight lines show two roughly linear regimes. (c) PCA analysis of Δ and (d) Ψ obtained from SPE measurements. RH dependence of principal components is shown in main plots with each component's contribution to the actual spectra shown in the insets. The units of Δ and Ψ are degrees and their principal components are displayed in relative units. Figure reproduced with permission.⁵⁵

double exponential fits shown in Figure 10(d). The ratio of A_2/A_1 corresponds to the relative activity of adsorbates at site 2 relative to site 1, while τ_2/τ_1 corresponds to the timescale associated with the adsorption rate at site 2 relative to the adsorption rate at site 1. At 10% RH, 97.5% of H₂O molecules adsorb rapidly at *Site-1* ($\tau_1 < 2$ minutes) while 2.5% adsorb at *Site-2* over the course of an hour ($\tau_2 \approx 50$ minutes). As RH increases, τ_1 increases by a factor of 3 while τ_2 does not undergo significant change, which results in a 3-fold increase in the occupancy of *Site -2* from 10% to 95% RH. The results strongly suggest that adsorption/desorption of water can be described by a double active site model that includes one strongly hydrophilic site which becomes quickly saturated as RH increases (*Site-1*) and one site which becomes more active as *Site-1* is filled (*Site-2*)¹²⁹. The hydrophilic site is associated with the Na⁺SO₃⁻ group, since this is the primary structure responsible for hydrophilicity/solubility of CuPcTs. Water saturation of the sulfonyl groups leads to dissociation of Na⁺ ions from SO₃⁻^{113, 115-116} and facilitates hydrogen bonding between water molecules until H₂O clusters merge, resulting in a multilayered meniscus containing mobile Na⁺ ions on the surfaces of CuPcTs domains. The site which becomes more active at high RH (*Site-2*) is likely related to diffusion of water into bulk CuPcTs domains and adsorption of water on previously-adsorbed water layers, which is driven by hydrogen bonding and van der Waals interaction between surface H₂O adsorbates and gas phase H₂O as well as H₂O coordination to electrical double layers formed by hydrated Na⁺ ions.¹³⁰

Modeling of adsorption kinetics

To model kinetics of the H₂O-CuPcTs interaction, we used pseudo-first order (PFO) and pseudo-second order (PSO) models to fit experimental H₂O adsorption curves⁵⁵. Single-site H₂O adsorption is modelled by the rate equation $dM_{ad}/dt = k'_2[H_2O_{vap}][M_e - M_t]$, where dM_{ad}/dt is the rate of mass

adsorption, k'_2 is the second order rate constant, $[H_2O_{vap}]$ is the concentration of H_2O vapor, and $[M_e - M_t]$ is the concentration of active adsorption sites (M_e is the mass adsorbed at equilibrium at a given P/P_0 and M_t is the mass adsorbed at time t at a given P/P_0). Under constant humidity conditions, $[H_2O_{ad}]$ is constant and can be absorbed into a new rate constant k_1 , where $k_1 = k'_2[H_2O_{vap}]$. The PFO rate equation then becomes $dM_{ad}/dt = k_1[M_e - M_t]$. Integration using the boundary condition $M_t(t = 0) = 0$ results in the linear form $\ln(M_e - M_t) = \ln(M_e) - k_1 t$. The plot of $\ln(M_e - M_t)$ vs. t is shown in Figure 10(a). The value of M_e was obtained from the equilibrium/saturation condition of each mass change. Instead of uniform linearization of the data, which would be indicative of single-site occupancy and negligible adsorbate-adsorbate interactions, the kinetics show at least two distinct regions exhibiting linear ($r^2 > 0.98$) behavior: one region with slope -0.2 to $-0.9 \ln(M_e - M_t)/\text{min}$ for fast adsorption ($t < 5$ min), and the second region exhibiting slope -0.020 to $-0.25 \ln(M_e - M_t)/\text{min}$ for slower adsorption ($t > 15$ min). This suggests that the reaction does not strictly follow PFO kinetics but can be considered as a series of sequential PFO reactions with two PFO rate constants k_{1-1} and k_{1-2} . Figure 11(b) shows k_{1-1} (left axis) and k_{1-2} (right axis) plotted as a function of vapor pressure. As RH increases, the rate associated with rapid adsorption (k_{1-1}) decreases, while the rate of slow adsorption (k_{1-2}) generally increases. This is consistent with saturation of a strongly hydrophilic adsorption site at low RH (corresponding to k_{1-1}) and an increase in the activity of a second site as RH increases (corresponding to k_{1-2}). The behavior of k_{1-1} and k_{1-2} resembles the trend in τ_2/τ_1 (Figure 10(d)). Both ratios τ_2/τ_1 and k_{1-2}/k_{1-1} increase linearly from ~ 0.03 to ~ 0.1 as RH increases from 10% to 95%, which suggests that the double exponential behavior modelled in Figure 10 represents 2 distinct sequentially-occurring PFO reactions. We estimated the fractional occupancy of *Site-2* predicted by the PFO model as $\theta_2 = M_{e2}/(M_{e1} + M_{e2})$, where M_{e1} and M_{e2} are the equilibrium masses extracted from the fitting the first and second linear regions in Figure 11(a). *Site-2* occupancy estimated from

double exponential and PFO kinetic models is shown in Figure 11(d) (bottom panel). Although θ_2 calculated from the PFO model is roughly a factor of 2 larger than θ_2 predicted from the double exponential model at high RH, both models predict that *Site-2* occupancy increases by a factor of 3-4 between 10% and 95% RH.

Results from double exponential and PFO kinetic models suggest that at least 2 distinct sites are active during H₂O adsorption on CuPcTs. To model the kinetics of 2-site adsorption¹³¹, we used the rate equation $dM_{ad}/dt = k'_2 [H_2O_{vap}] [M_{e1} - M_{t1}] [M_{e2} - M_{t2}]$, where k'_3 is the third order rate constant, M_{ei} is the mass adsorbed at equilibrium at a given P/P_0 at site i and M_{ti} is the mass adsorbed at time t at a given P/P_0 at site i . Under constant humidity conditions, $[H_2O_{ad}]$ is constant and absorbed into a new rate constant k_2 , where $k_2 = k'_3 [H_2O_{vap}]$. In the approximation $[M_{e1} - M_{t1}] \approx [M_{e2} - M_{t2}]$, the pseudo-second order (PSO) rate equation¹³² becomes $dM_{ad}/dt = k_2 (M_e - M_t)^2$. After integration using the boundary condition $M_t(t = 0) = 0$, the linear form of the PSO rate equation is $t/M_t = 1/k_2 M_e^2 + t/M_e$. Linear fits to the plots of t/M_t vs. t achieve $r^2 > 0.998$ inside the entire measured RH range (Figure 11(c)), indicating that the value of ΔM closely follows PSO reaction kinetics due to the presence of 2 different adsorption sites.

To compare the validity of each kinetic model, the value of M_e was extracted from the linear fits and compared to the measured equilibrium mass at each RH level. Figure 11(d) (bottom panel) shows $|\Delta M_e|$, the percent difference between measured and predicted equilibrium mass by each model. For the PFO reaction model, we used $M_e = M_{e1} + M_{e2}$. The PSO model predicts the equilibrium mass with $< 3\%$ error, while the double exponential model achieves $< 5\%$ error. The PFO model exhibits the highest average error ($\sim 10\%$) because it does not account for the possibility of multiple adsorption sites. The rate constant k_2 was

extracted and compared to k_{1-1} and k_{1-2} .⁵⁵ Although the units for first and second order rate constants are different, the PSO rate constant k_2 clearly resembles behavior of the PFO rate constant k_{1-1} , and its value lies between the values of k_{1-1} and k_{1-2} because k_2 describes a combination of two sequentially-occurring reactions with rates k_{1-1} and k_{1-2} . Thus, even while the H₂O-CuPcTs interaction most closely follows PSO kinetics due to multiple adsorption sites, useful information about the reaction kinetics is obtained by modeling the reaction as a series of sequential PFO reactions. Since kinetics of desorption exhibited double exponential behavior (Figure 10(c)) and showed no significant dependence on water vapor pressure, desorption kinetics were not analyzed in terms of PFO and PSO models.

Optical response to humidity

Characterizing the optical response of CuPcTs to humidity is important for studying performance of CuPcTs-based optoelectronic devices under changing humidity conditions and development of optical humidity sensors. Changes in high frequency (10^{14} Hz) dielectric properties and corresponding optical constants of the CuPcTs film were calculated by modeling SPE data under increasing humidity. Figure 12(a) shows extinction coefficient (k) (top panel) and index of refraction (n) (bottom panel) as a function of wavelength (λ) at different RH levels. Water exposure leads to significant decreases in k between 550 and 650 nm and decreases in n between 450 and 900 nm. Peak positions of the B- and Q-bands shift to lower energies and the probability of $\pi \rightarrow \pi^*$ transitions decrease by 50% as RH increases from 3% to 90%. Changes in the slopes of n and k with RH indicate the presence of a 2-step process.⁵⁵ The values of n (measured at 450 and 650 nm) decrease slowly for RH < 60% and drop sharply at RH > 60%. Similar behavior is observed in the RH dependence of k .⁵⁵ The observed changes are likely related to dielectric screening of the CuPcTs film by

dipolar water^{130, 133-134}. At low RH, the film's dielectric response to H₂O adsorption is weak, since delocalization of π -electrons in the phthalocyanine ring allows high electronic polarizability and dielectric constant¹³⁵. At RH > 60%, water saturation of CuPcTs domains leads to dielectric screening of the CuPcTs electronic charge carriers by dipolar water layers, which results in dramatic decreases in the values of n and k.

Optical absorption spectra of CuPcTs were used to estimate optical bandgap energies of the B- and Q-bands (Figure 12(b) bottom panel) using a Tauc plot.⁵⁵ Insignificant change occurs in bandgap energy for RH < 60% RH, but sharp decreases in both B-band and Q-band bandgap energies occur at RH > 60%, indicating formation of lower energy states which emerge after H₂O saturation of CuPcTs domain surfaces has occurred. This result, related to the behavior of n and k, is caused by dielectric screening of CuPcTs by water. Optical thickness of the CuPcTs film was estimated from SPE data. Exposure to H₂O vapor increases CuPcTs film thickness by a factor of 3 as RH is increased from 3% to 90% (Figure 12(b) top panel). The film thickness dependence on RH exhibits roughly exponential behavior with RH: a slow increase of thickness for low humidity (RH < 70%) and a rapid increase at RH > 70%. The CuPcTs optical thickness change also exhibits slight (~10 nm) hysteresis in the 50-80% RH range between adsorption and desorption processes. The rapid thickness change at RH > 70% is consistent with formation of a mixed H₂O-CuPcTs phase facilitated by hydrogen bonding between H₂O adsorbates and gas-phase water molecules.^{40, 116-117} Upon formation of H₂O multilayers and merging of adjacent adsorbed H₂O clusters, interactions between mobile Na⁺ ions, CuPc(SO₃⁻)₄,¹¹⁵ and hydrogen-bonded water can facilitate fracture and displacement of solid-phase domains which increases intermolecular spacing and leads to significant film swelling.^{56, 91,}

136-137

To investigate the source of dramatic changes that occur in optical constants at $RH \approx 70\%$, we performed statistical analyses of Δ (phase difference) and Ψ (amplitude ratio) obtained from SPE measurements.⁵⁵ Application of principal component analysis (PCA) revealed that Δ contains 2 major principal components (Figure 12(c)). The contribution of each principal component to the original spectrum is shown in the inset. At $RH < 30\%$, the spectrum is a result of a single component. At $RH \approx 30\%$, a second component appears and its contribution to Δ grows as RH increases. At $RH > 70\%$, component-2 becomes dominant and forms 100% of the contribution to Δ at $RH > 90\%$. Similar behavior is observed in Ψ , which shows contributions from at least 3 components (Figure 12(d)). While the concentration of component-3 remains relatively constant throughout the measured RH range, the component-2 fraction increases sharply at $RH \approx 60\%$. The PCA results support proposed adsorption kinetics models, which indicate that a secondary adsorption process occurs after H_2O saturation of strongly hydrophilic sites. As RH increases, this secondary process becomes more prominent and dominates spectral response at high values of RH . PCA results indicate that significant changes in optical constants which occur near 60-70% RH are a result of the emergence of a secondary process which becomes active after significant H_2O adsorption has taken place in the film, which suggests that the secondary principal component is related to dielectric screening caused by H_2O saturation of CuPcTs domains.

Electrical response to humidity

The most common phthalocyanine-based humidity sensors rely on measurement of direct-current (DC) electrical resistivity measurements. Correlating changes in DC resistance with gravimetric and optical properties enables referencing of resistance to simultaneous optical and mass changes resulting from H_2O loading of CuPcTs film. Figure 13(a) shows relative changes in the DC resistance (R/R_0)

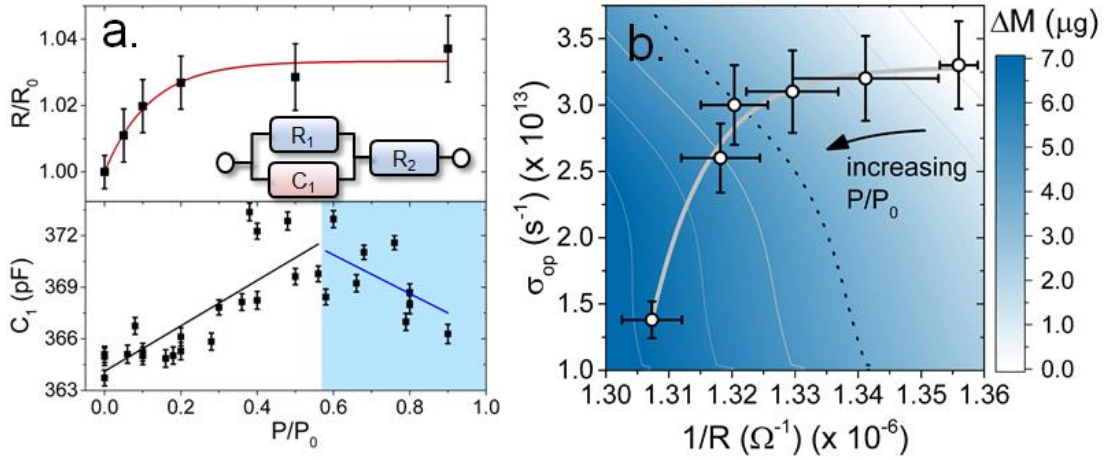


Figure 13. (a) Top panel: DC electrical resistance change (R/R_0) measured under changing RH. Red curve is exponential fit. Error bars correspond to uncertainty in R/R_0 due to low signal to noise ratio. Inset: equivalent circuit used to model EIS data. Bottom panel: Capacitance extracted from equivalent circuit model shows transition at $\sim 60\%$ RH. Error bars are propagated from errors in fitting to equivalent circuit model. (b) Relationship between optical conductivity (σ_{op}) and electrical conductivity (represented by $1/R$, where R is the DC resistance), plotted with mass change (ΔM) of the CuPcTs film during uptake of water and an exponential fit (gray curve). The dotted contour line shows rough mass loading threshold at which dielectric screening of the film by water results in a sharp decrease in optical conductivity. Error bars are propagated from measurements of R/R_0 and extraction of ϵ_2 by fitting to the Lorentz oscillator model. Figure reproduced with permission.⁵⁵

as RH is increased. The value of R/R_0 exhibits roughly exponential behavior, reaching equilibrium at ~50% RH, which suggests that water adsorption alters DC conductivity of the film only before water saturation of CuPcTs domain surfaces has occurred. The adsorption of water onto previously adsorbed H₂O clusters or multilayers in the mixed H₂O-CuPcTs phase at RH > 60% does not further affect carrier mobility. The DC resistance increases linearly with mass during H₂O adsorption⁵⁵. The film exhibits a small (~3%) change in DC resistance between vacuum and 90% RH compared to non-sulfonated CuPc, which can show conductivity changes of up to 50% under similar RH conditions⁵⁷.

To further investigate electrical response of CuPcTs, EIS was performed to study dielectric properties of the CuPcTs film in the 1 Hz – 8 MHz frequency range during exposure to H₂O. A Nyquist plot of imaginary vs. real impedance⁵⁵ shows a suppressed single semi-circle, suggesting that a modified Randles equivalent circuit model is appropriate for fitting (inset in Figure 13(a))¹³⁸. Fitting was performed on impedance spectra measured from 0% to 90% RH. Both R_1 and R_2 undergo slight changes at RH $\approx$ 57%.⁵⁵ The value of R_1 corresponds to the film resistance and changes insignificantly. The value of R_2 corresponds to resistance at the film-electrode interface and exhibits a small transition near RH $\approx$ 57%. At low RH, H₂O interaction with hydrophilic sulfonyl groups facilitates intercalation of water between CuPcTs domains and electrodes, slowly increasing resistance at the film-electrode interface. At RH > 60%, the formation of H₂O layers containing mobile Na⁺ ions can increase the effective contact area at electrodes and result in improved electronic transport by allowing charge carriers to hop between hydrated ionic structures consisting of coordinated Na⁺ and dipolar H₂O, leading to a decrease in R_2 . Film capacitance (C_1) exhibits a sharp change at RH $\approx$ 60% (Figure 13(a) bottom panel). At low RH, capacitance increases due to an increase in average dielectric constant caused by adsorption of H₂O and the formation of electrical double layers composed of hydrated Na⁺ ions. At RH > 60%, the value of C_1 begins decreasing. This is related to higher mobility of

ions and film domains as the water-CuPcTs matrix enters a mixed H₂O-CuPcTs phase¹¹³. The increased mobility facilitates the breakdown of electrical double layers and a resultant decrease in capacitance.

To compare the effect of humidity on electrical and optical conductivities, we extracted optical conductivity (σ_{op}) from SPE spectra using the imaginary dielectric constant (ϵ_2) by $\sigma_{op} = \epsilon_2 \omega / 4\pi$, where ω is the optical frequency.⁵⁵ Optical conductivity was calculated at 600 nm (corresponding to the maximum absorbance of Q-band of CuPcTs) and reflects RH dependence at this wavelength. We used $1/R$ as a measure of electrical conductivity, where R is the DC resistance. Since electrical conductance ($1/R$) differs from electrical conductivity (ρ) by a constant factor related to electrode spacing ($\rho = RA/l$, where A is the cross-sectional electrode area and l is the channel length between electrodes), the effect of humidity on conductance can be used as an equivalent measure of its effect on conductivity. Figure 13(b) shows electrical ($1/R$) and optical (σ_{op}) conductivities and relates them to mass change of CuPcTs as the film undergoes water adsorption. The effect of water on electrical conductivity is most pronounced at low RH, when water clustering around hydrophilic moieties hinders electronic charge carrier hopping between adjacent CuPcTs molecules. At ~60% RH (represented by dotted contour line), optical conductivity exhibits a sharp decrease due to the onset of dielectric screening of the CuPcTs domains by a water meniscus and hydrated ionic double layer structures^{130, 133-134}.

The transition in C_1 occurs in the same RH range (50-70%) at which significant changes in optical constants, bandgap, and film thickness occur. As RH increases, contribution of the first adsorption mechanism (water on CuPcTs) decreases, and a secondary process (water adsorption on H₂O-CuPcTs) becomes prevalent. This is consistent with the results from the adsorption kinetics models which suggest that multiple PFO reactions are active during H₂O adsorption on CuPcTs. The combination of these results strongly suggests that

H₂O adsorption on CuPcTs can be described in terms of two sequentially-occurring PFO reaction steps. During the first step, H₂O molecules undergo rapid adsorption at hydrophilic sulfonyl/salt groups near CuPcTs domain surfaces. Crowding of adsorbates near these groups facilitates salt dissociation leading to formation of 4 Na⁺ ions and negatively charged CuPc(SO₃⁻)₄. During the second step (illustrated in Figure 14), slow H₂O adsorption onto previously adsorbed H₂O clusters/layers and diffusion into CuPcTs crystallites results in formation of interconnected channels that allow Na⁺ mobility. Hydrogen bonding between adsorbed water molecules mediated by van der Waals interactions results in formation of a phase which contains mobile H₃O⁺, Na⁺, and CuPc(SO₃⁻)₄ ions. The appearance of this mixed H₂O-CuPcTs phase is associated with pronounced changes in optoelectronic and structural properties of the film, and dielectric screening of CuPcTs at optical frequencies. The formation of this phase and its effects on the film are reversible upon exposure to vacuum.

Multimodal humidity detection sensitivity

Figure 15(a) summarizes the results of CuPcTs RH sensitivity as estimated using different measured modes. Here, sensitivity refers to the smallest RH changes detectable by the measurement technique at a given water vapor pressure P/P_0 as estimated from the signal to noise ratio (SNR) for each response. We compare the RH response of capacitance C_1 (AC impedance spectroscopy in the 1 Hz – 8 MHz frequency range), relative resistance change R/R_0 (DC resistivity), n (optical constant in 300 – 700 THz range), and ΔM (gravimetric QCM-based measurements). Capacitance response exhibits the lowest sensitivity (~10% RH) at $P/P_0 < 0.2$ as a result of low SNR. As RH increases, sensitivity of R/R_0 to humidity decreases exponentially due to saturation of R/R_0 at ~30% RH (Figure 13(a)). The sharp increase in ΔM which occurs for $P/P_0 < 0.4$ (Figure 10(b))

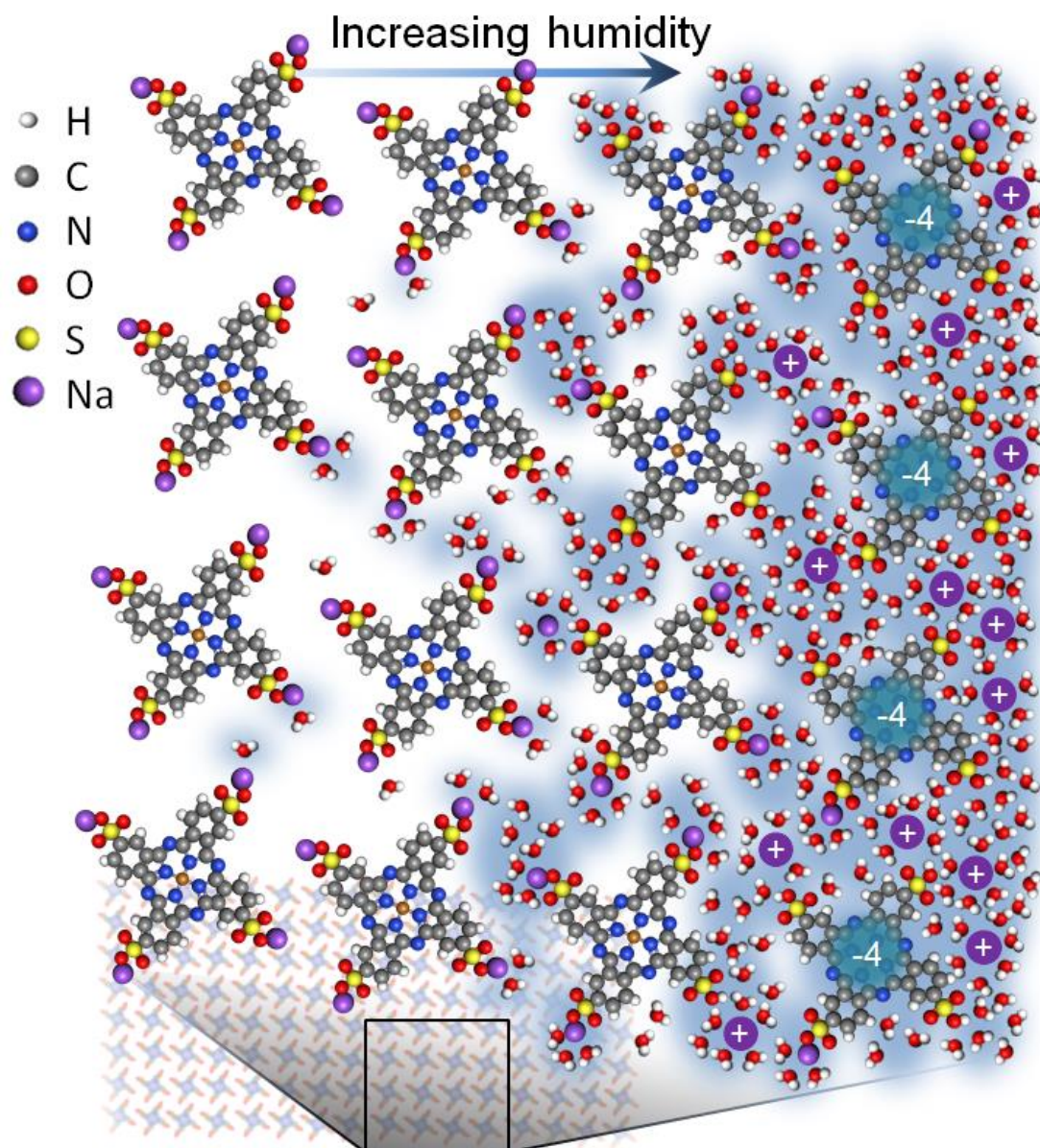


Figure 14. Water crowding at hydrophilic sulfonyl/salt groups leads to dissociation of Na^+ ions from $\text{Na}_4\text{CuPc}(\text{SO}_3)_4$. At $\text{RH} > 60\%$, water clusters begin to merge, which allows ion diffusion throughout the water-saturated film. Mobile Na^+ ions are represented by purple (+) symbols while $\text{CuPc}(\text{SO}_3)_4$ ions are left with -4 charges. Figure reproduced with permission.⁵⁵

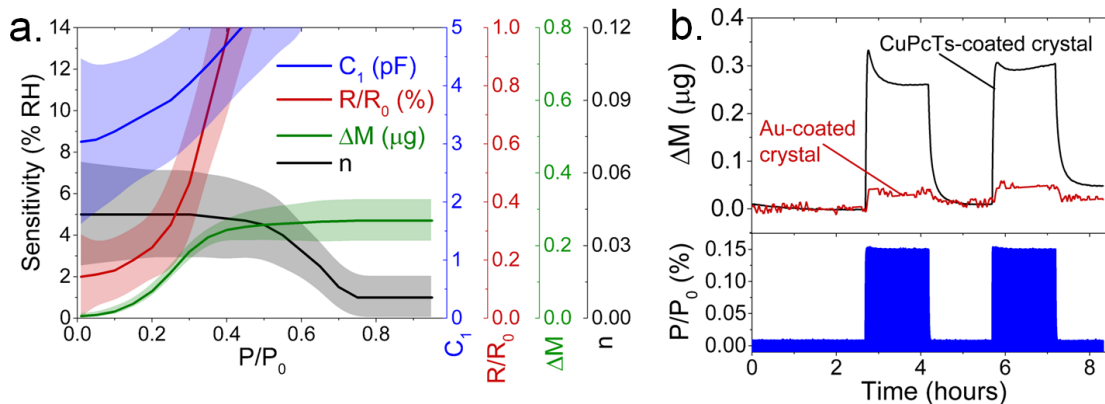


Figure 15. (a) Estimated RH sensitivity achieved by measuring capacitance (C_1), DC resistivity (R/R_0), QCM frequency shift (ΔM), and optical constants (n) for RH sensing. Shaded regions represent uncertainty range. Right axes show estimated measurement sensitivity of each technique. Axes units are shown in plot legend. (b) Top panel: display of RH sensing limit of mass-based measurements showing ΔM as calculated from frequency shift of CuPcTs-coated QCM crystal (black) and bare gold-coated crystal (red). Bottom panel: Two pulses of H_2O vapor corresponding to $\sim 0.15\%$ RH which is detected using CuPcTs-coated QCM. Figure reproduced with permission.⁵⁵

allows for high resolution ($< 2\%$ RH) sensing under low humidity conditions. At $\text{RH} > 40\%$, ΔM shows reduced sensitivity of about 4.5% RH due to linear response. This trend is opposite to that of n (optical-mode sensing), which exhibits high RH dependence at $P/P_0 > 0.6$ (Figure 12(a))⁵⁵ and thus represents the most sensitive ($< 2\%$ RH) detection mode at high RH. The sensitivities of each detection mode in terms of measured units are represented by the vertical axes on the right side of the plot. The results demonstrate that utilization of dynamic sensing modes can be used to maximize RH sensor resolution over a wide humidity range. We find that mass-based measurements achieve the highest resolution at $\text{RH} < 50\%$ while optical techniques achieve the highest resolution at $\text{RH} > 50\%$. To estimate the detection limit at which the highest-resolution sensing mode can be demonstrated, we measured mass response of the CuPcTs film when exposed to $\sim 50 \times 10^{-3}$ mbar pulses of H_2O vapor, which correspond to $\sim 0.15\%$ RH. Figure 15(b) shows the CuPcTs-coated and bare gold-coated QCM response to 0.15% RH exposure. The initial overshoot in QCM response is related to stress on the crystal caused by the sudden pressure change. The CuPcTs-coated crystal shows sensitivity corresponding to $\sim 0.1\%$ RH. Our findings demonstrate the possibility of using water-soluble materials for flexible, printable humidity sensors which can employ a combination of electrical, optical, or mass-based sensing mechanisms for maximizing humidity sensitivity across the entire $\sim 0\text{-}95\%$ RH range.

Conclusions

We studied the interaction of H_2O vapor with film of CuPcTs using a multimodal approach which links gravimetric, broadband dielectric spectroscopy, and DC electrical resistivity measurements. Pseudo-first order, pseudo-second order, and double exponential fits were used to model kinetics of H_2O adsorption on CuPcTs film. Results indicate that the H_2O -CuPcTs interaction can be described

by two-step pseudo-first order kinetics. The first step is associated with adsorption of H₂O on hydrophilic sulfonyl sites at the periphery of CuPcTs grains. Adsorption at these sites does not lead to significant changes in optoelectronic properties of the film. The second process becomes distinguishable at RH > 60% and is related to H₂O saturation of CuPcTs surface sites and diffusion of water into bulk CuPcTs grains. Formation of a percolated H₂O network leads to higher mobility of Na⁺ ions and subsequent changes in optical properties and dielectric screening of CuPcTs domains by H₂O and mobile ions at high frequencies. Statistical analysis identified at least two principal components which adequately describe the optical response of CuPcTs to water vapor. Finally, we demonstrate the value of using a multimodal approach for understanding mechanisms of sensing and referencing optical and electrical changes to the mass of adsorbed water on the surface of the sensor, as well as identification of the most sensitive detection modes for analyte identification. A combination of gravimetric and optical detection modes was selected to enable the highest resolution ($\pm 2.5\%$ RH) humidity sensing in the entire 0-95% RH range, with gravimetric detection as the most sensitive mode for RH < 50% and optical detection as most sensitive for RH > 50%.

Chapter 5: Oxygen, humidity, UV light response of CNTs

A version of this chapter was originally published By Eric Muckley, Anthony Nelson, Christopher Jacobs, and Ilia Ivanov:

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Abstract

Interaction between UV light and carbon nanotube (CNT) networks plays a central role in gas adsorption, sensor sensitivity, and stability of CNT-based electronic devices. To determine the effect of UV light on sorption kinetics and resistive gas/vapor response of different CNT networks, films of semiconducting single wall nanotubes (s-SWNTs), metallic single wall nanotubes (m-SWNTs), and multiwall nanotubes (MWNTs) were exposed to O₂ and H₂O vapor in the dark and under UV irradiation. Changes in film resistance and mass were measured in situ. In the dark, resistance of metallic nanotube networks increases in the presence of O₂ and H₂O, whereas resistance of s-SWNT networks decreases. UV irradiation decreases the resistance of metallic nanotube networks in the presence of O₂ and H₂O and increases the gas/vapor sensitivity of s-SWNT networks by nearly a factor of 2 compared to metallic nanotube

networks. s-SWNT networks show evidence of delamination from the gold-plated quartz crystal microbalance (QCM) crystal, possibly due to preferential adsorption of O₂ and H₂O on gold. UV irradiation increases the sensitivity of all CNT networks to O₂ and H₂O by an order of magnitude, which demonstrates the importance of UV light for enhancing response and lowering detection limits in CNT-based gas/vapor sensors.

Introduction

Carbon nanotubes (CNTs) belong to a family of carbon allotropes that are being explored for application in transparent conducting electrodes¹³⁹⁻¹⁴⁰, photovoltaics¹⁴¹, LEDs¹⁴², transistors¹⁴³, biointerfaces¹⁴⁴, and gas sensors¹⁴⁵. Their unique optoelectronic properties and compatibility with roll-to-roll processing have brought carbon-based materials to the forefront of nanoscience research¹⁴⁶. The bandgap of semiconducting carbon nanotubes (s-CNTs) can be further tuned with intrinsic and extrinsic dopants¹⁴⁷. However, the stability of CNT devices in humid and oxygen rich environments may present a fundamental limitation to reliable device performance. The high surface area of CNTs facilitates adsorption of gas molecules such as water and oxygen which can alter band gap and work function, local density of states, and induce charge transfer and semiconductor-metal transitions¹⁴⁸⁻¹⁵⁰.

The perfect sp² hybridization in defect-free graphene makes it electronically stable and generally prevents strong chemical adsorption of atmospheric gases¹⁴⁹. The curvature of fullerenes and nanotubes on the other hand introduces sp³ character to the dominant sp² planar C=C bonding¹⁴⁶. Disruption of the perfect sp² network significantly increases the reactivity of nanostructures. Exposure of CNT networks to oxygen and humidity leads to charge transfer with O₂ and H₂O adsorbates¹⁴⁸⁻¹⁵³. Rapid desorption of O₂ and H₂O from film surfaces

is critical for the reversibility of CNT sensors and strongly affects the surface wetting characteristics of CNT networks¹⁴⁸⁻¹⁵⁰. Thermal treatment is often used for the removal of physisorbed molecules, but in CNTs it may promote material decomposition, resulting in the formation of CO and CO₂ products rather than O₂ desorption¹⁵⁴. Partial CNT oxidation disrupts sp² bonding and leads to the formation of locally electron-rich and electron-deficient regions/defects, facilitating the formation of COOH, OH, and CO functional groups^{149, 155}. Besides thermal treatment, UV irradiation can be used for desorption of adsorbates and control of wetting properties^{149, 153}. Continuous UV irradiation of CNTs leads to the formation of structural defects, electronic photoexcitation¹⁵⁴, and photoinduced plasmons in the CNTs¹⁵⁶⁻¹⁵⁷. This combination of processes makes it difficult to identify the primary mechanisms that mediate adsorption/desorption processes under UV irradiation, which generally improves the resistive response of CNTs¹⁵⁵.

Density function theory (DFT) calculations show that physisorbed O₂ molecules orient with O=O bonds parallel to CNT surfaces¹⁵³. This leads to hybridization between the valence bands of CNTs and O₂ acceptor molecules which increases the density of states at the Fermi level¹⁵² and results in hole doping behavior¹⁵⁴. Oxygen molecules physisorb strongly (with binding energy of ~0.25 eV) on SWNTs, withdrawing about e/10 charge per each adsorbed molecule¹⁵⁸. Similar response to O₂ was reported for MWNT¹⁵⁵, C₆₀¹⁵⁹⁻¹⁶¹, and other graphene-derived structures^{157-158, 162}. Desorption of O₂ under UV irradiation is primarily mediated by photo-generated π -electron surface plasmons¹⁵⁵. Plasmon lifetime in SWNTs is on the order of 1 fs, after which plasmons decay into single-particle hot electron and hole excitations¹⁶³. Photoinduced plasmon energy of hot carriers can overcome the activation energy (E_A) barrier of O₂ adsorption^{156, 158}. Hot carrier injection has been proposed as one of the primary mechanisms of UV photodesorption of O₂ and other electron-accepting adsorbates from SWNT, MWNT, and graphene^{155, 157}.

UV irradiation also enhances dissociative chemisorption of O₂ and H₂O on carbon surfaces. Singlet oxygen can be formed by UV photoexcitation of gas-phase triplet O₂ or by interactions between physisorbed triplet O₂ and UV photoexcited carbon allotropes¹⁵⁵. Exposure to singlet O₂ generally leads to the oxidation of CNT networks^{160, 164}. During dissociative chemisorption of oxygen, each O atom rests above a C=C bond bridge site to form a C-O-C complex which destroys the perfect π -bonding between carbon atoms. It remains unclear whether this enhances further photooxidation at other C-C bridge sites¹⁵³⁻¹⁵⁴ due to disruption of π -bonding or leads to chemical stabilization of the nanostructure by trapping local photoinduced charge carriers^{155, 160}.

Dissociative chemisorption of H₂O becomes favored over O₂ when oxygen or hydrogen defects are present on the CNT surface. UV-enhanced removal or addition of C-H and C-OH groups formed by H₂O dissociation allows for control of reversible hydrophobic-hydrophilic transitions on the surface¹⁵³, where the OH moiety acts as an electron acceptor, behaving similarly to physisorbed O₂¹⁴⁹. Charge transfer to H₂O and OH has been observed in SWNT¹⁵² and C₆₀¹⁵⁹ and can lead to bandgap opening in graphene by up to 0.2 eV^{150, 153}.

Photoinduced adsorption/desorption processes can be described in terms of electronic excitations in CNTs in the presence of electron acceptors such as O₂ or H₂O, as shown in Figure 16(d). E_{A1} represents the energy barrier to charge transfer from the CNT to an electron acceptor (O₂/H₂O), and E_{A2} is the energy barrier to electron transfer from the acceptor to the CNT. O₂ approaches the CNT in its spin triplet ground state, where the O-O bond has a binding energy of 5.2 eV, the highest occupied molecular orbital (HOMO) is the π^*_{2p} level, and the lowest unoccupied molecular orbital (LUMO) is the σ^*_{2p} level¹⁶⁵. In the dark, E_{A1} corresponds to the work function of the carbon surface (~4.8 eV for defect-free SWNT bundles¹⁶⁶ and 4.7 eV for defect-free C₆₀¹⁶⁷), and adsorption of O₂ is primarily mediated by van der Waals interactions. For purely van der Waals-

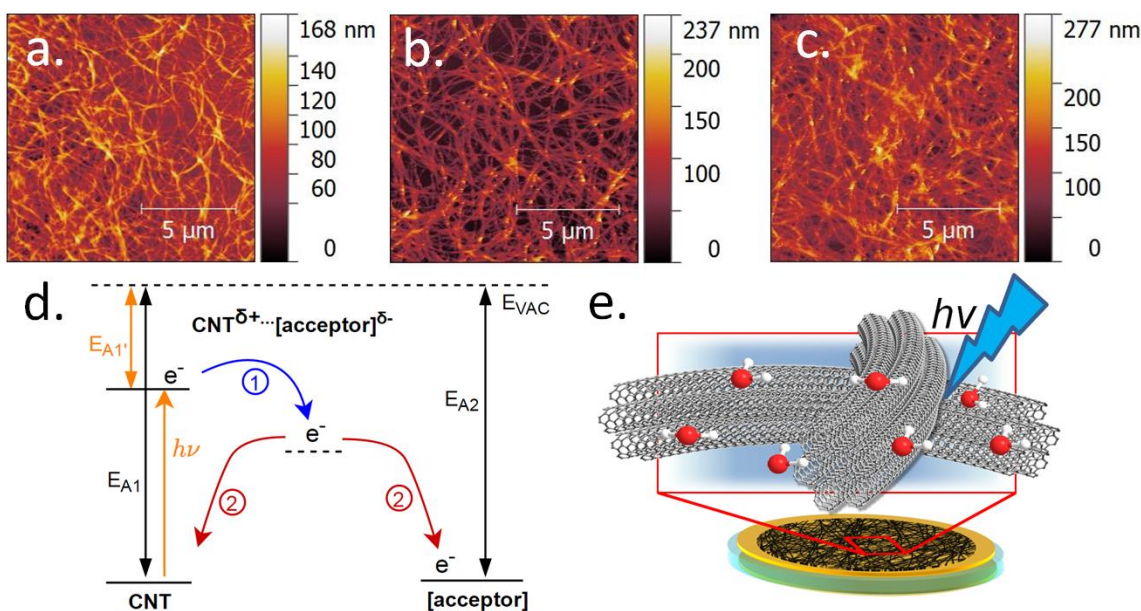


Figure 16. AFM images of (a) s-SWNT, (b) m-SWNT, and (c) MWNT networks. d. Schematic of photoinduced adsorption and desorption of electron-accepting O_2 and H_2O on CNTs. The energy barrier to electron transfer to (E_{A1}) and from (E_{A2}) the charge transfer complex (CNT^{δ+} ... [acceptor]^{δ-}) are decreased under UV irradiation, resulting in enhancement of both photoinduced chemisorption (1) and photoinduced molecular desorption (2). e. Schematic of H_2O adsorption and photoinduced desorption from a junction between two bundles of (5,5) SWNT bundles on a gold-plated QCM crystal. Figure reproduced with permission.⁵⁹

induced adsorption processes, O_2 remains in its triplet ground state and $E_{A1} = 0$. However, the presence of structural defects enables charge transfer between O_2 and SWNT with $E_{A1} \approx 1.2$ eV^{155, 168}. Physical adsorption of O_2 results in pinning and broadening of the O_2 LUMO level to the Fermi level (E_F) of the CNT, effectively decreasing the energy barrier E_{A1} and increasing the probability of charge transfer complex $[CNT^{\delta+} \cdots O_2^{\delta-}]$ formation¹⁶⁹. The formation of this unstable intermediate state is denoted by (1), while desorption is denoted by (2).

Under UV irradiation, photon absorption in CNTs may promote E_F level electrons by as much as 3.5 eV, leading to electron hole pair production and plasmon generation, which facilitate electron transfer from the CNT to physisorbed O_2 by reducing E_{A1} to $E_{A1'}$. In semiconducting carbon structures, adsorption-induced bending of the valence and conduction bands causes charge carriers to migrate in opposite directions. In p-type CNTs, UV absorption enhances downward band bending since the surface photovoltage (SPV) transports negative charge to the film surface¹⁷⁰. The SPV effect narrows the effective width of the E_A barrier, increasing the probability of charge transport back and forth across the barrier. Excitation in the adsorbed O_2 molecule by singlet quenching of the CNT surface or by direct absorption of UV photons¹⁵⁵ lowers the effective height of E_{A2} , which increases the probability of electron transfer from adsorbed O_2 back to the CNT, facilitating molecular desorption. Since UV irradiation effectively lowers energy barriers E_{A1} and E_{A2} , both molecular adsorption and desorption rates may be enhanced in the presence of UV light.

Figure 16(a-c) shows atomic force microscope (AFM) images of the s-SWNT, m-SWNT, and MWNT networks, respectively. The CNTs exist in ~ 100 nm diameter bundles over $10 \mu m$ long in uniformly dispersed networks. Some impurities are visible in the m-SWNT and MWNT networks. Figure 16(e) shows a schematic of H_2O adsorption on a junction between two bundles of (5,5) SWNTs. The strong van der Waals interaction between nanotubes is perturbed upon gas/vapor

adsorption, allowing gas migration between bundles, which may affect CNT-QCM adhesion at the QCM interface. Adsorption of charge-accepting molecules alters the conductivity of the tubes as well as the tube-tube junctions, which results in the strong electronic gas/vapor response of SWNTs and MWNTs.

Experiment

We studied the effect of UV irradiation on the electrical resistance of s-SWNT, m-SWNT, and MWNT networks in humid and oxygen rich environments.

Adsorption/desorption of O₂ and H₂O on CNT networks was measured using a quartz crystal microbalance (QCM). S-SWNTs and m-SWNTs were purchased from Nanointegris. Dispersion of SWNTs was prepared by ultrasonication in toluene for 1 hour. MWNTs (99% pure) were purchased from Cheap Tubes Inc. and purified by nitric acid reflux. MWNTs were mechanically mixed in dimethylformamide (DMF) and sonicated for 30 minutes. The SWNT and MWNT solutions were drop-cast on AT-cut gold-plated QCM crystals and on Si/SiO₂ substrates with gold interdigitated electrodes (IDEs). Substrates were pre-cleaned by sonicating in acetone for 30 minutes. Substrates were weighed with 0.1 µg resolution using a UMX2 microbalance (Mettler Toledo) before and after solution casting to determine the mass of each deposited CNT film. Data collected during the experiment (QCM frequency shift and film resistance) was normalized by CNT film mass in order to compare the response between different networks. AFM images of CNT networks were acquired using an Asylum Research Cypher S AFM in tapping mode with conductive Pt/Ir-coated cantilever operated at 73 MHz resonance frequency.

Prior to measurements, networks were placed under vacuum of 10⁻⁶ Torr for 3 hours to desorb contaminants. During the experiment samples were exposed to 5, 10, 15, and 20 Torr pulses of H₂O vapor and O₂ which were injected into the

vacuum chamber using a gas control manifold. Electrical resistance of the networks was measured in a 4-point probe configuration with a Keithley 6430 source-meter. Frequency shift of the QCM crystal was measured using an SRS QCM200 5 MHz quartz crystal microbalance system. Gas flow control, electrical, and mass measurements were integrated and controlled using LabVIEW software. The experiment was performed in the dark and under UV irradiation from a Hg lamp filtered through the quartz window of the vacuum chamber. The QCM data were corrected for the response of an empty QCM crystal under the same experimental conditions.

Results and discussion

Figure 17 shows mass change (ΔM) of CNT networks exposed to 5, 10, 15, and 20 Torr pulses of O₂ (a) and H₂O vapor (b) in the dark and under UV radiation. Resistance change (R/R_0) of the CNT networks during the same gas/vapor sequences is shown in Figure 17(c) for O₂ and Figure 17(d) for H₂O. In m-SWNT and MWNT, mass sorption on CNT networks is irreversible upon exposure to vacuum, both in the dark and under UV irradiation. UV irradiation leads to enhancement of the resistive gas/vapor response by roughly an order of magnitude in all CNT networks, although the effect of UV irradiation O₂/H₂O adsorption/desorption kinetics varies across networks.

Since ΔM and R/R_0 response kinetics are largely independent of the pressure of the gas/vapor pulse and the magnitude of response is roughly proportional to the pressure, it is useful to compare the response of each CNT network during the 20 Torr pulse. At the beginning of the 20 Torr pulse, mass and resistance of CNT networks have not fully recovered from the previous gas/vapor pulses. However, ΔM and R/R_0 response kinetics are similar during every gas/vapor pulse, including the 5 Torr pulse, in which CNT networks were fully recovered from

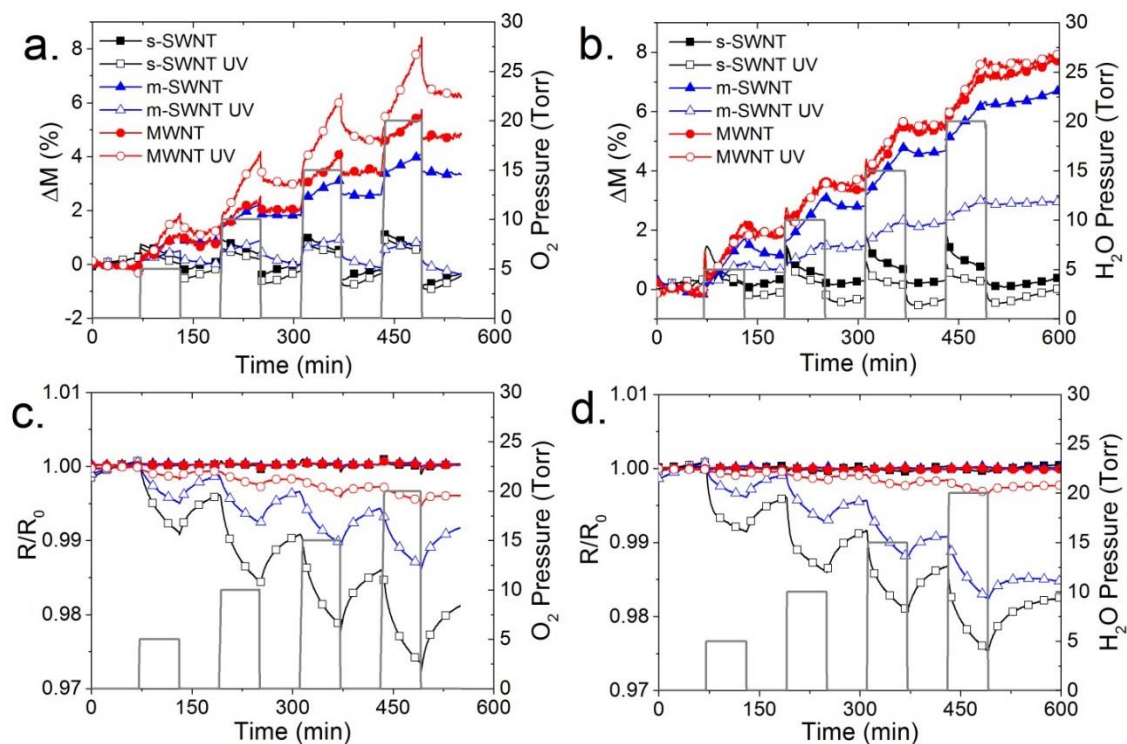


Figure 17. (a) Mass change (ΔM) of CNT networks when exposed to 5, 10, 15, and 20 Torr pulses of O_2 in the dark and under UV irradiation. (b) ΔM when CNT networks are exposed to 5, 10, 15, and 20 Torr pulses of H_2O in the dark and under UV irradiation. (c) Resistance change (R/R_0) of CNT networks when exposed to pulses of O_2 in the dark and under UV irradiation. (d) Resistance change (R/R_0) of CNT networks when exposed to pulses of H_2O in the dark and under UV irradiation. In (c) and (d), $|R/R_0| < 0.05\%$ for s-SWNT, m-SWNT, and MWNT networks in the dark. Figure reproduced with permission.⁵⁹

previous experiments. This suggests that significant changes in ΔM and R/R_0 response kinetics do not occur as a result of incomplete recovery. Therefore, we describe response kinetics during the 20 Torr pulse in terms of fully-recoverable CNT networks. CNT responses are compared during the 20 Torr gas/vapor pulse by subtracting background mass and normalizing resistance so that $\Delta M = 0$ and $R/R_0 = 1$ when the 20 Torr pulse begins. ΔM of the CNT networks exposed to 20 Torr pulses of O_2 (a) and H_2O vapor (b) are shown in Figure 18. Adsorption of both O_2 and H_2O on s-SWNT, m-SWNT, and MWNT networks leads to rapid initial mass increase in the dark and under UV irradiation.

Upon initial exposure to H_2O , mass of the MWNT network first increases quickly, then decreases, then increases further, but more slowly. The apparent rapid increase and decrease of ΔM within the first 2 minutes of the pulse are likely a consequence of abrupt pressure changes or condensation of H_2O on the QCM crystal but are not necessarily related to H_2O adsorption on the MWNT network since the MWNT resistance exhibits a monotonic decrease. The gradual increase in ΔM in m-SWNT and MWNT networks after the initial gas/vapor adsorption step is likely a result of diffusion of O_2 and H_2O into the CNT network. The decrease in ΔM after the initial increase in s-SWNT is discussed further below.

MWNT and m-SWNT networks exhibit similar behavior in the dark. However, UV irradiation increases the rate of oxygen diffusion into the MWNT film by a factor of 2 without significant change in the desorption kinetics. This suggests that UV-induced charge transfer from MWNTs to physisorbed oxygen facilitates chemisorption which cannot be reversed by exposure to vacuum, even under UV irradiation. Oxygen adsorption on m-SWNT is inhibited under UV irradiation. In m-SWNTs, delocalization of conduction electrons enhances the generation of UV-induced plasmons which facilitate molecular desorption of O_2 by hot carrier injection.

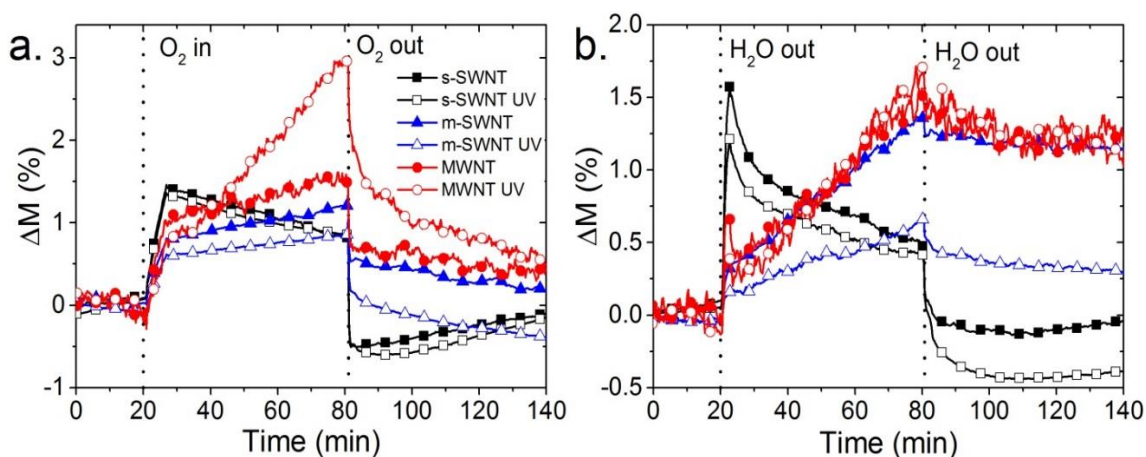


Figure 18. Change in mass (ΔM) of semiconducting SWNT (s-SWNT), metallic SWNT (m-SWNT), and MWNT networks when networks are exposed to a 20 Torr pulse of O_2 (a) and H_2O (b) in the dark (solid shapes) and under UV irradiation (open shapes). Introduction and removal of gas/vapor is marked by vertical dotted lines. Figure reproduced with permission.⁵⁹

As shown in Figure 18(b), desorption of H₂O from m-SWNTs and MWNTs occurs over a time scale of roughly 10 hours. Less than half of adsorbed H₂O is desorbed after networks have been placed under vacuum for 1 hour, even under UV irradiation. Water molecules that are hydrogen-bonded to C-H and C-OH groups are readily desorbed under vacuum. This makes up less than 20% of the total H₂O adsorbed. Since UV irradiation does not affect the H₂O adsorption/desorption kinetics on MWNTs, it suggests that the H₂O-MWNT interactions are not strongly affected by photoinduced processes. The irreversible H₂O chemisorption observed on MWNTs occurs primarily through interactions with CNT defects, since the energy barrier to H₂O chemisorption cannot be overcome by charge transfer from defect-free MWNTs.

UV irradiation strongly decreases the rate of H₂O adsorption and diffusion into the m-SWNT network. Irradiation generates surface plasmons which result in hot carrier injection into O₂ and H₂O adsorbates, stimulating desorption¹⁶³. The time constant for gas desorption is on the order of hours, which suggests that the energy density of photoinduced plasmons in m-SWNTs is below the energy barrier required for facilitating rapid desorption of chemisorbed OH and H groups.

Interestingly, 5 min. after the start of the O₂ pulse, mass of the s-SWNT film begins to decrease linearly (Figure 18(a)). Over the course of the 60-minute O₂ pulse, roughly 30% of the initial mass is lost. A similar decrease in mass is observed 2 min. after the H₂O pulse begins, in which 70% of the initially adsorbed H₂O mass is lost (Figure 18(b)). Similar behavior was observed for s-SWNT upon exposure to 5, 10, and 15 Torr O₂/H₂O pulses. Since the decrease in mass is observed in the dark as well as under UV irradiation, it is not likely caused by photodesorption processes. At first glance, the data suggest that after the initial adsorption step, a different desorption process takes place while the s-SWNT film is still exposed to gas/vapor during the same pulse. However, monotonically-changing film conductivity (see s-SWNT data in Figure 19)

demonstrates that adsorption increases continuously throughout the entire duration of the gas/vapor pulse. We propose that the apparent decrease in mass is evidence of partial delamination of the s-SWNT film from the surface of gold-plated QCM crystal. Since individual SWNTs are bundled primarily as a result of van der Waals interactions, adsorption of O₂ or H₂O on bundled tubes disrupts tube-tube adhesion. As O₂/H₂O molecules diffuse to the film-gold interface, intercalation of adsorbates between s-SWNTs and gold may result disruption of the tube-gold adhesion and cause partial delamination of s-SWNTs from the QCM crystal due to preferential adsorption of O₂ and H₂O on gold. Delamination facilitates slipping between the s-SWNTs and gold as the crystal oscillates at ~5 MHz. This reduces the effective mass of the film bound to the crystal, increasing the resonance frequency of the crystal. Since the decrease in mass is observed during each gas/vapor pulse, we propose that delamination of the s-SWNT film from the gold surface is reversible and occurs 2-5 min. after gas/vapor exposure. This description is consistent with the observation that changes in mass become negative ($\Delta M < 0$) after gas/vapor evacuation. Desorption of oxygen from the s-SWNT/QCM interface leads to slow recovery of the of gold-nanotube adhesion. The effect of H₂O on s-SWNT delamination is more pronounced than that of O₂ primarily because of hydrogen bonding between H₂O intercalates at the s-SWNT/gold interface.

The change in electrical resistance of CNTs exposed to 20 Torr pulses of O₂ (a) and H₂O (b) in the dark and under UV irradiation are shown in Figure 19. Prior to the gas/vapor pulse, $R/R_0 < 0$ for metallic CNTs due to lack of full recovery from the previous pulse 15 Torr pulse. The time constant of the resistance response is not strongly influenced by the pressure of the gas/vapor. The resistance of s-SWNT, m-SWNT, and MWNT networks changes by less than 0.05% in response to 20 Torr pulses of O₂ and H₂O in the dark. Under UV irradiation, the magnitude of the gas/vapor response increases by more than a factor of 10. The strong enhancement of gas response by UV irradiation is consistent with results

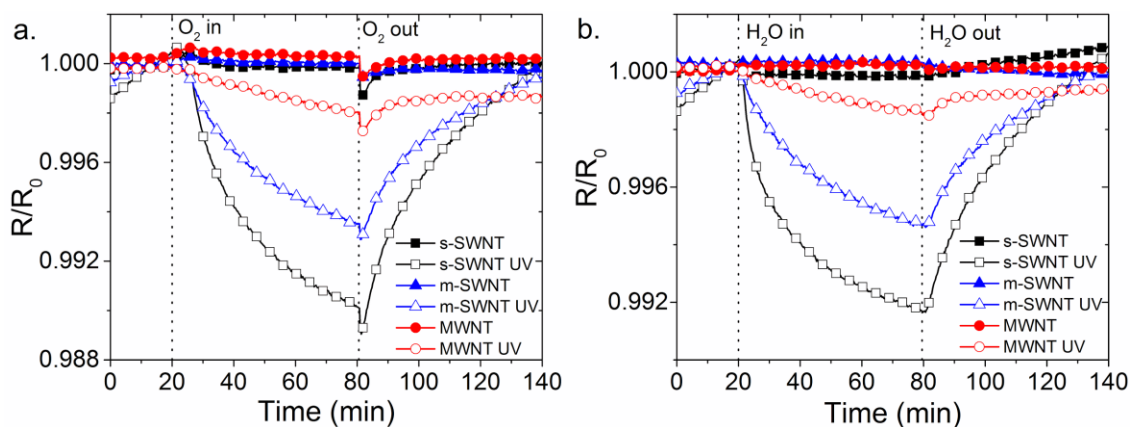


Figure 19. Resistance change (R/R_0) of semiconducting SWNT (s-SWNT), metallic SWNT (m-SWNT), and MWNT networks when networks are exposed to a 20 Torr pulse of O_2 (a) and H_2O (b) in the dark (solid shapes) and under UV irradiation (open shapes). Introduction and removal of gas/vapor is marked by vertical dotted lines. Prior to the gas/vapor pulse, $R/R_0 < 1$ for metallic CNTs due to lack of full recovery from the previous pulse. Figure reproduced with permission.⁵⁹

reported in the literature¹⁷¹. The weak reversible gas response that occurs when networks are kept in the dark suggests that significant charge transfer does not occur between O₂/H₂O and CNTs in the absence of UV irradiation. In MWNTs, UV irradiation increases both the rate of O₂ adsorption and the magnitude of the resistance response. This suggests that enhancement of the resistance response occurs mainly because more O₂ is adsorbed under UV irradiation. However, UV irradiation enhances the MWNT resistance response to H₂O without increasing H₂O adsorption on the film, so it is likely that the resistance response enhancement is related to photogenerated charge carriers, not additional vapor adsorption in the case of H₂O.

The UV-enhanced decrease in resistance in s-SWNTs upon exposure to both O₂ and H₂O confirms that both molecules behave as electron acceptors. Defect-free s-SWNTs lack free charge carriers at E_F¹⁷² but charge transfer from s-SWNTs to adsorbates leaves holes which contribute to charge transport resulting in a drop of film resistance. In both s-SWNTs and m-SWNTs, the resistance response to O₂ and H₂O is reversible. UV irradiation inhibits reversibility of the MWNT gas/vapor resistive response. This is consistent with the results in Figure 17 and Figure 18, which shows that the O₂/H₂O adsorbed on MWNT during the gas/vapor pulses does not fully desorb under vacuum conditions. It is likely that formation of charge transfer complexes between O₂/H₂O and MWNT result in the irreversible gas binding. In MWNTs, Cao et al. observed chemisorption of reducing gases which open a gap between E_F and the valence band, resulting in the formation of a Schottky barrier at the film surface¹⁷³. This explanation is consistent with our results since we observe a resistance drop upon exposure to acceptor adsorbates.

The magnitude of the resistance response (ΔR) of the CNT networks is shown as a function of gas/vapor pressure in Figure 20(a) for O₂ and Figure 20(b) for H₂O. For clarity, the horizontal dotted lines denote $\Delta R=0$. The electronic response to

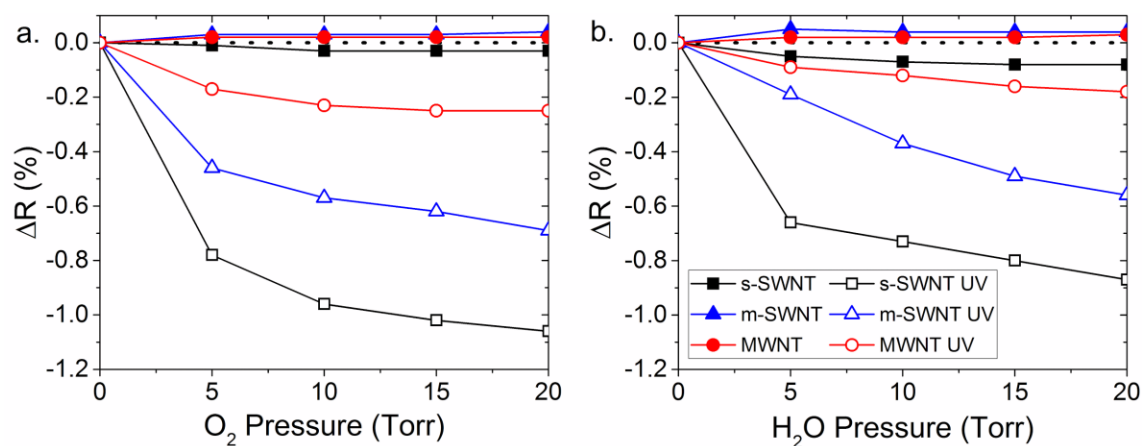


Figure 20. Resistance response (ΔR) to O_2 (a) and H_2O (b) as a function of gas/vapor pressure in the dark (solid shapes) and under UV irradiation (open shapes). $\Delta R=0$ is denoted by the dotted horizontal line. Figure reproduced with permission.⁵⁹

O₂ as a function of pressure is qualitatively like that of H₂O. An important result in Figure 20 is that $\Delta R > 0$ in m-SWNTs and MWNTs upon exposure to gas/vapor in the dark, but $\Delta R < 0$ under UV irradiation. The change in the sign of ΔR under UV irradiation suggests that the dominant mechanism of the resistive gas/vapor response changes when photoinduced processes are active. Similar behavior of the m-SWNTs and MWNTs confirms metallic behavior of the MWNT film due to delocalization of conduction band electrons. The adsorption of electron-accepting O₂ and H₂O on these networks leads to charge carrier depletion in the film surface, increasing the resistance. Under UV irradiation, electrons are photoexcited to conduction bands in the depleted region leaving behind holes which contribute to charge transport. Consequently, UV irradiation induces p-type behavior in metallic CNTs when electron acceptor adsorbates are present on the film. Since s-SWNTs exhibit p-type behavior, adsorption of acceptor molecules in the dark increases the film conductivity, as seen in Figure 20(a) and (b). Under UV irradiation, electronic photoexcitations result in an increase in valence band holes, further increasing the film conductivity.

The data shown in Figure 17(c) and (d) were extrapolated to estimate the limits of H₂O and O₂ detection for each CNT network in the dark and under UV irradiation. Detection limits are defined as minimum gas/vapor pressures required to induce resistance changes of $> 0.2 \Omega$ in the CNT network. For reference, the lowest H₂O detection limit reported here for s-SWNT under UV irradiation corresponds to $0.20 \pm 0.08\%$ relative humidity. The detection limits drop by roughly an order of magnitude or more when CNT networks are exposed to UV irradiation⁵⁹. This suggests that while UV irradiation is important for improving gas/vapor sensor sensitivity, it also decreases the electronic stability of CNT films undergoing sorption by ambient gas/vapor molecules.

Conclusions

Interaction between O_2 and H_2O and CNT networks depends on the nature of nanotubes (semiconducting, metallic). In metallic nanotubes, O_2 and H_2O adsorption decreases concentration of mobile charge carriers (electrons), resulting in higher resistance due to formation of $(CNT^{\delta+} \cdots [acceptor]^{\delta-})$ charge transfer complex. In s-SWNT networks, the effect is opposite due to p-type behavior. UV irradiation reverses the sign of majority charge carriers in metallic nanotubes and under O_2 and H_2O exposure the network resistance decreases. In s-SWNT networks, the nature of majority charge carriers does not change, and adsorption of electron acceptors further increases the conductivity of the network. In s-SWNT, we find evidence of adsorption-induced disruption of CNT adhesion to gold electrodes. We propose that the effect is reversible and stems from perturbation of van der Waals interaction between tubes and preferential adsorption of electron acceptors on gold, which leads to partial delamination of s-SWNTs from the QCM surface. We find that UV irradiation increases the resistive response and decreases the detection limits of s-SWNT, m-SWNT, and MWNT networks by roughly an order of magnitude. This demonstrates the importance of UV irradiation for improving the sensitivity of gas/vapor sensors and elucidates the role of UV irradiation on the environmental stability of CNT-based devices.

Chapter 6: Humidity response of PEDOT:PSS

A version of this chapter was originally published by Eric Muckley, Christopher Jacobs, Keith Vidal, J.P. Mahalik, Rageev Kumar, Bobby Sumpter, and Ilia Ivanov:

Muckley, E.S., Jacobs, C.B., Vidal, K., Mahalik, J.P., Kumar, R., Sumpter, B.G. and Ivanov, I.N., 2017. New insights on electro-optical response of poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) film to humidity. *ACS applied materials & interfaces*, 9(18), pp.15880-15886.

Spectroscopic ellipsometry was performed by Christopher Jacobs and Keith Vidal. Computational modeling was performed by Jyoti Prakash Mahalik, Rajeev Kumar, and Bobby Sumpter. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Abstract

Understanding the relative humidity (RH) response of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is critical for improving the stability of organic electronic devices and developing selective sensors. In this work combined gravimetric sensing, nanoscale surface probing, and mesoscale optoelectronic characterization are used to directly compare the RH dependence of electrical and optical conductivities and unfold connections between the rate of water adsorption and changes in functional properties of PEDOT:PSS film. We report three distinct regimes where changes in electrical conductivity, optical conductivity, and optical bandgap are correlated with the mass of adsorbed water. At low (RH < 25%) and high (RH > 60%) humidity levels dramatic changes in electrical, optical and structural properties occur, while changes are insignificant in mid-RH (25% < RH < 60%) conditions. We associate the three regimes with water adsorption at hydrophilic moieties at low RH,

diffusion and swelling throughout the film at mid-RH, and saturation of the film by water at high RH. Optical film thickness increased by 150% as RH was increased from 9% to 80%. Low frequency (1 kHz) impedance increased by ~100% and film capacitance increased by ~30% as RH increased from 9% to 80% due to an increase in the film dielectric constant. Changes in electrical and optical conductivities concomitantly decrease across the full range of RH tested.

Introduction

Advances in flexible electronics facilitate the development of personal wearable sensors for environmental monitoring and biometrics¹⁷⁴. The polymer mixture poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is suitable for use as a low-cost wearable relative humidity (RH) sensor because of its resistive RH response¹⁷⁵, compatibility with inkjet printing¹⁷⁶, and mechanical flexibility¹⁷⁷⁻¹⁷⁸. Its hygroscopic nature however limits the stability of flexible optoelectronic devices¹⁷⁹⁻¹⁸⁰, as exposure to water can alter electronic¹⁸¹⁻¹⁸², optical¹⁸³, morphological¹⁸⁴, and viscoelastic properties of PEDOT:PSS^{40, 185-187}. Despite the importance of PEDOT:PSS in flexible sensors, electrodes¹⁸⁸⁻¹⁸⁹, and soft actuators¹⁹⁰⁻¹⁹¹, the structure of the film, the mechanism of charge carrier transport, and correlation between optical, electronic, and mechano-structural responses to RH remain poorly understood¹⁹². Unfolding these relationships is critical for understanding sensing mechanisms in PEDOT:PSS and improving selectivity, sensitivity, and durability of wearable RH sensors and other PEDOT:PSS-based devices.

The PEDOT:PSS polyelectrolyte complex consists of a phase segregated structure in which ~30 nm diameter conductive PEDOT-rich polycationic domains are encapsulated by ~1 nm thick PSS-rich polyanionic shells¹⁸⁶. The domains are embedded in an electronically insulating PSS matrix loosely-crosslinked by

hydrogen bonding¹⁹³. In the presence of water vapor, H₂O molecules adsorb directly onto hydrophilic PSS sulfonic acid groups:

$\text{H}_2\text{O} + \text{PSS}(\text{HSO}_3) \rightarrow \text{H}_3\text{O}^+ + \text{PSS}(\text{SO}_3)^-$.¹⁹⁴ Additional water molecules hydrogen bond to less active PSS sites and previously-adsorbed H₂O molecules facilitating prompt diffusion of water into the film¹⁸³⁻¹⁸⁴. Hydrogen bonding between water molecules strains existing hydrogen bonds in the PSS matrix which leads to inter-domain decoupling and decohesion of the PEDOT:PSS complex, decreasing rigidity of the polymer matrix, and swelling of the film.¹⁹⁴ Loading of water to the point of saturation may lead to irreversible morphological changes and increases in film thickness by 75% under some conditions^{183, 195}, while showing only 2% volume change in other experiments¹⁹⁶. The degree of film swelling is dependent on experimental conditions, the ratio of PEDOT to PSS in the film, film aspect ratio, and the presence of dopants. Strong van der Waals and hydrogen bonding between water molecules becomes a dominant force after H₂O monolayer formation¹⁹⁶ and exposure to RH levels above 80% leads to H₂O multilayer formation and condensation on the PEDOT:PSS surface^{175, 179}.

PEDOT:PSS is most often used as a hole transport layer in organic electronic devices, and recently transport of ions injected from electrolyte solutions was studied¹⁹⁷. The conductivity of PEDOT:PSS at RH < 30% is thought to be mediated by mobility of holes between conductive PEDOT-rich domains. The hydrophilic PSS electrolyte contains anionic immobile sulfonic acid groups and protons (hydronium ions) as counter ions. At RH > 30%, water loading of PSS chains permits hopping of the protons between sulfonic acid groups¹⁸³, which may lead to increased charge mobility. At the same time, water-induced swelling of the PSS matrix increases separation between adjacent PEDOT domains, reducing charge carrier concentration^{179, 193}. The mechanism of charge transport and how adsorption of water affects dielectric response of PEDOT:PSS film across a broad frequency range is still unclear. To examine these questions we studied electrical and optical RH responses of PEDOT:PSS films *in situ*. For the

first time, we complement gravimetric and optoelectronic measurements of water adsorption on the macro scale with nanoscale probing of PEDOT:PSS surface potential to unfold connections between the rate of water adsorption and changes in electrical and optical properties of the film. Since the current study focuses on high frequency dielectric response of the PEDOT:PSS film which is dominated by electronic conductivity, the effect of water adsorption on ionic conductivity in PEDOT:PSS films was not investigated in detail here.

Experiment

Conductive grade PEDOT:PSS (0.5% PEDOT, 0.8% PSS by wt.) was acquired from Sigma Aldrich. This particular composition was chosen as the subject of study because of its high conductivity and optical transparency, which makes a material of choice for transparent electrode applications in thin film photovoltaic and top gate field-effect devices. AT-cut gold-plated 5 MHz quartz crystal microbalance (QCM) crystals and Si/SiO₂ substrates with and without silver interdigitated electrodes (IDEs) were cleaned by sonication in acetone for 30 minutes. PEDOT:PSS solution was spin-cast at 3000 RPM for 60 seconds to obtain ~50 nm thick films on all substrates. Atomic force microscope (AFM) and Kelvin probe force microscope (KPFM) images were acquired using an Asylum Research Cypher S AFM in tapping mode with conductive Pt/Ir-coated cantilever operated at 73 MHz resonance frequency. All AFM and KPFM measurements were performed inside a controlled gas environment chamber. Humidity was controlled using an L&C RH200 humidity generator by mixing water vapor with dry N₂. The film was allowed to equilibrate for 2 hours before each image was acquired. Spectroscopic ellipsometry (SPE) was performed using a J. A. Woollam Co. variable-angle ellipsometer in the 450-1000 nm wavelength range. During SPE measurements, RH was controlled using a specially-designed gas flow cell. A Zahner IM6 electrochemical workstation was used to perform *in situ*

electrochemical impedance spectroscopy (EIS) during the SPE measurements. After relative humidity was increased, the film was allowed to stabilize and equilibrate with the environment for 30 minutes prior to DC electrical resistance, QCM, EIS, and SPE measurements.

Prior to vacuum-based measurements, films were placed under vacuum of 10^{-6} Torr (1.33×10^{-6} mbar) for 3 hours. Samples were exposed to increasing H₂O vapor pressures while frequency shift of the QCM crystal was measured using an SRS200 QCM controller and resistance measurements were performed with a Keithley 2420 source-meter *in situ*. The QCM frequency shift was corrected by subtracting the shift from a bare gold-coated QCM crystal to remove the effect of H₂O adsorption on gold. Water vapor was injected into the vacuum chamber using a mass flow controller (MFC). The MFC, source-meter, and QCM oscillator were controlled using LabVIEW software. Vacuum based experiments were performed in a modified Dynamic Vapor Sorption system from Surface Measurement Systems.

Results and discussion

Nanoscale response to humidity

An AFM image of the PEDOT:PSS film at ambient humidity is shown in Figure 21(a). The film contains regions of aggregated grains resulting in a rough (root-mean-square roughness ~ 8.5 nm) surface. Figure 21(b) shows cross-sections of the surface profile at 30%, 50%, and 93% RH. The cross-section region is represented by the white bar on the AFM image in the inset. As RH increases, the profiles show an increase in film height relative to the height of the tallest feature. The water-induced film swelling is consistent with swelling reported in

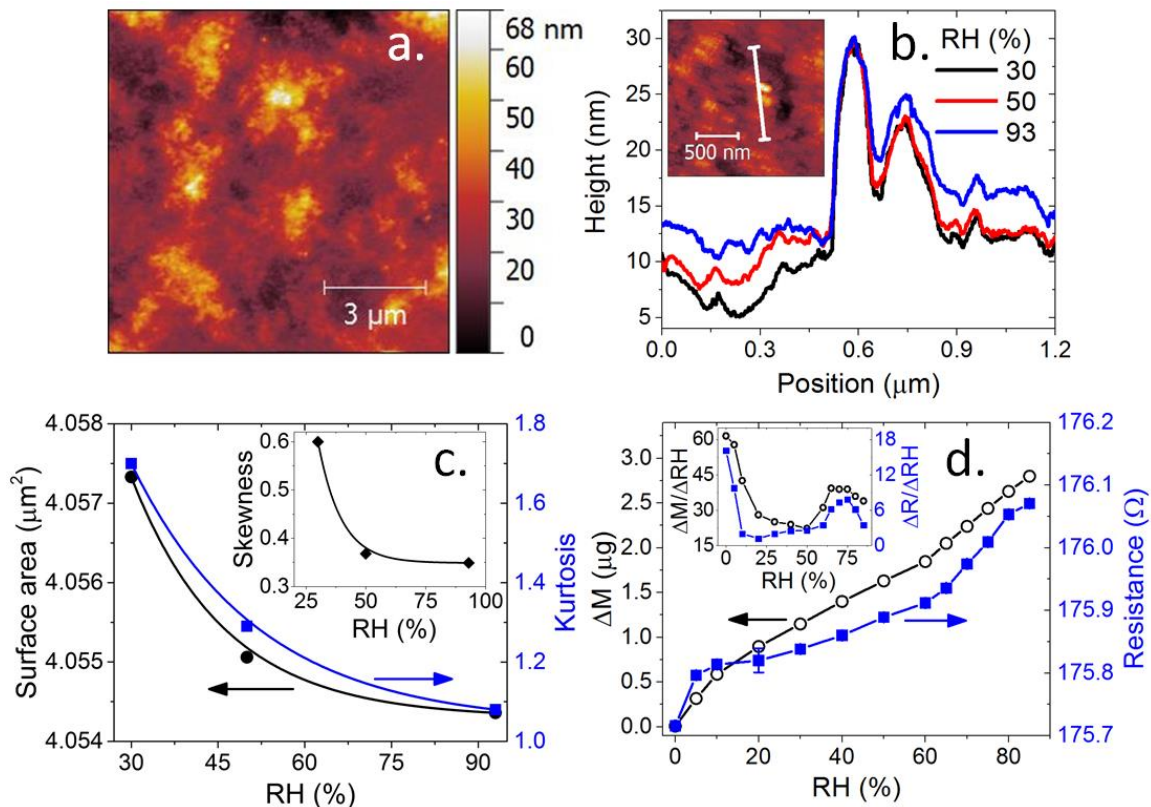


Figure 21. (a) AFM image of PEDOT:PSS film at ambient humidity. (b) Cross-section of PEDOT:PSS film at 30%, 50%, and 93% RH. Average height of the film surface increases relative to the height of the tallest feature with increasing RH. Inset shows the cross section region. (c) Statistical analysis of the image in (b) at 30%, 50%, and 93% RH. Inset: skewness in the surface height distribution. (d) Mass change (ΔM , black open circles) and electrical resistance (solid blue squares) of PEDOT:PSS at different RH levels. Inset: average rate of change in mass ($\Delta M/\Delta RH$) and average rate of change in resistance ($\Delta R/\Delta RH$) as a function of changing RH levels. The units of $\Delta M/\Delta RH$ are [$\text{ng}/\%RH$], and $\Delta R/\Delta RH$ units are [$\text{m}\Omega/\%RH$]. Figure reproduced with permission.⁵⁶

other studies^{183, 195}. The most notable swelling occurs at RH = 93%, which is likely due to H₂O multilayer formation observed by others in PEDOT:PSS films at RH > 80%^{175, 179}. Since filling of small (< 50 nm) inter-domain regions by water is not easily resolved in the AFM image, homogenization of the film surface is best represented using a statistical approach, in which surface area, skew, and kurtosis of the images were calculated and plotted in Figure 21(c). The curved lines are exponential fits. With increasing RH, the surface area, kurtosis, and skewness in height distribution (inset) decrease. As water crowding occurs on the film surface, capillary action facilitates the filling of inter-grain crevices by H₂O. The formation of an H₂O meniscus on the PEDOT:PSS surface leads to further homogenization of the surface, resulting in reduced surface area. The third and fourth standardized moments of the height distribution are skewness and kurtosis, respectively. For a Gaussian distribution, kurtosis is equal to $3\sigma^4$, where σ is the standard deviation. The decrease in kurtosis with increasing RH corresponds to a general homogenization of the film surface, where the height deviations of both high outliers (peaks) and low outliers (micropores) are decreased as H₂O adsorption takes place on the film. Skewness represents a measure of the asymmetry in the height distribution. Skewness > 0 indicates that the histogram of height values visible in the AFM image is skewed to the right. This corresponds to a film in which the height of the primary outlier features is greater than the average film height, as opposed to a porous or pitted film surface (skewness < 0). As RH increases, the skewness decreases towards 0. This indicates that film swelling reduces the difference between the average film height and the height of the tallest features, consistent with the cross-section profiles in Figure 21(b).

Simultaneous gravimetric and electrical resistance measurements show that water sorption on PEDOT:PSS increases mass and electrical resistance of the film (Figure 21(d)). Average rate of change in mass ($\Delta M/\Delta RH$, [ng/%RH]) and rate of change in resistance ($\Delta R/\Delta RH$, [m Ω /%RH]) are shown in the inset. The

values of $\Delta M/\Delta RH$ and $\Delta R/\Delta RH$ were calculated using the difference between adjacent points in Figure 21(d) to give a rough estimate of the humidity regimes in which mass adsorption and electrical resistance exhibit the highest response to changes in RH. At least three distinct regimes are visible between 3% and 93% RH. Both $\Delta M/\Delta RH$ and $\Delta R/\Delta RH$ are highest for RH < 20%. Exposure of PEDOT:PSS to H₂O vapor at low RH levels results in rapid adsorption of water at hydrophilic HSO₃ sites, leading to correlated significant change in both ΔM and ΔR as the PSS matrix undergoes initial water uptake and swelling. For 20% < RH < 60%, both $\Delta M/\Delta RH$ and $\Delta R/\Delta RH$ remain low, indicating that the mass loading rate slows as adsorption sites become crowded by H₂O molecules. At RH > 60%, the magnitudes of $\Delta M/\Delta RH$ and $\Delta R/\Delta RH$ increase by nearly a factor of two. It is likely that this is a result of multilayer H₂O formation on the film surface after active sites become saturated with H₂O. Surface water forms hydrogen bonds with molecules in the gas phase leading to an increase in the mass loading rate as reported by QCM. It is likely that the decrease in $\Delta M/\Delta RH$ and $\Delta R/\Delta RH$ observed at RH > 80% occur as a result of equilibrium between adsorption and desorption of water molecules from the H₂O-saturated film surface.

Results of KPFM measurements are shown in Figure 22 with topography of the imaged area shown in the inset of Figure 21(b). Statistical analysis of KPFM images in (b) shows that as RH increases from 3% to 93%, average surface potential increases by ~50%. The charged AFM tip induces image charges in the PEDOT:PSS film which alter electrostatic potential outside the film by a term $-e/4\epsilon x$,¹⁹⁸ where ϵ is the dielectric constant of the film and x is the distance to the film surface. Uptake of water into the PEDOT:PSS matrix increases the film's average dielectric constant (ϵ), which results in higher potential on the surface due to the smaller induced image charge. Surface potential variation across the measured area decreases by ~10% as RH increases from 3% to 93% (right y-axis in (b)). The dipole moment of water compensates dipoles on the PEDOT:PSS surface, which decreases work function of the film and leads to

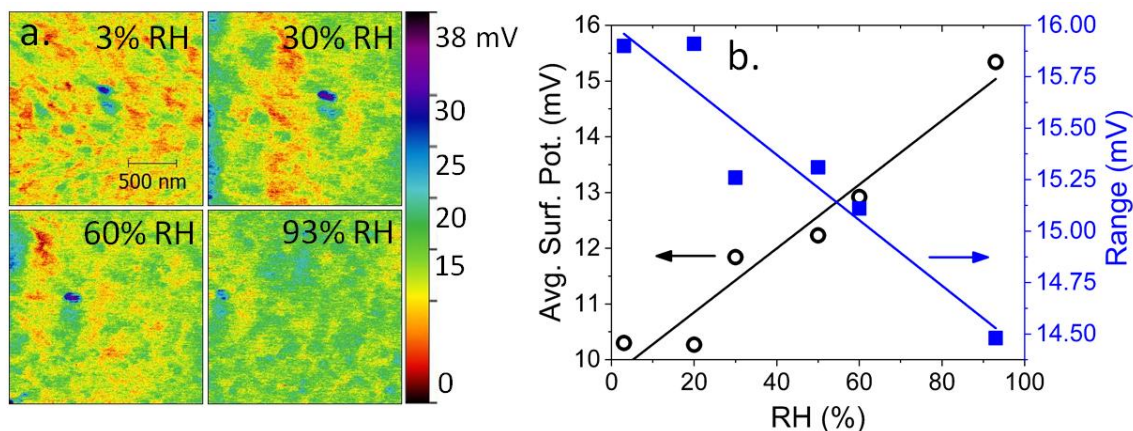


Figure 22. (a) Surface potential of PEDOT:PSS film at 3%, 30%, 60%, and 93% RH. The image area is the same as that shown in Figure 21(b) inset. (b) Statistical analysis of KPFM images shown in (a). Average surface potential increases and the range of measured surface potential values decreases as water sorption leads to homogenization of the surface. Figure reproduced with permission.⁵⁶

screening of the polymer complex from the AFM tip, resulting in an increasingly uniform surface potential. Surface potential homogenization caused by water sorption has been observed in oxide films as well⁵⁸.

AC electrical response to humidity

Water interaction with PEDOT:PSS which leads to formation of hydronium ions changes the concentration of mobile ions in the film. Conductivity of PEDOT:PSS is commonly explained in terms of electron/hole hopping but it is likely that mixed ionic and electronic charge transport occurs^{183, 197}. Figure 23 shows the dielectric response of PEDOT:PSS film to changing RH levels in (a) Nyquist (imaginary impedance (Z'') vs. real impedance(Z')) and (b) Bode plot (impedance vs. frequency) representations. Symbols represent experimental data and solid lines show fits to the equivalent circuit model. We used a modified Randles equivalent circuit for modelling multi-step adsorption of water on polymer film containing both ionic and electronic charge carriers (inset in (b))¹⁹⁹⁻²⁰¹. The equivalent circuit contains contributions from shunt resistance (R_s), film capacitance (C_f), ionic charge resistance (R_{ion}), and an RC element representing diffusion/transport across boundaries with charge transfer resistance (R_{ct}) and film/electrode interface capacitance (C_e). Low frequency ($< 10^4$ Hz) impedance increases by nearly 100% as RH is increased from 9% to 80%, likely due to swelling of the PSS matrix which increases the distance between conductive PEDOT domains¹⁹⁴.

Figure 23 (a) and (b) show RH-dependence of real (Z') and imaginary (Z'') impedance of the PEDOT:PSS film as measured at 1 kHz, 500 kHz, and 1 MHz. From 3% to 85% RH, Z' nearly doubles at 1 kHz while staying relatively constant ($Z' \approx 120 \Omega$) at 1 MHz. The RH dependence of Z' decreases as the frequency is

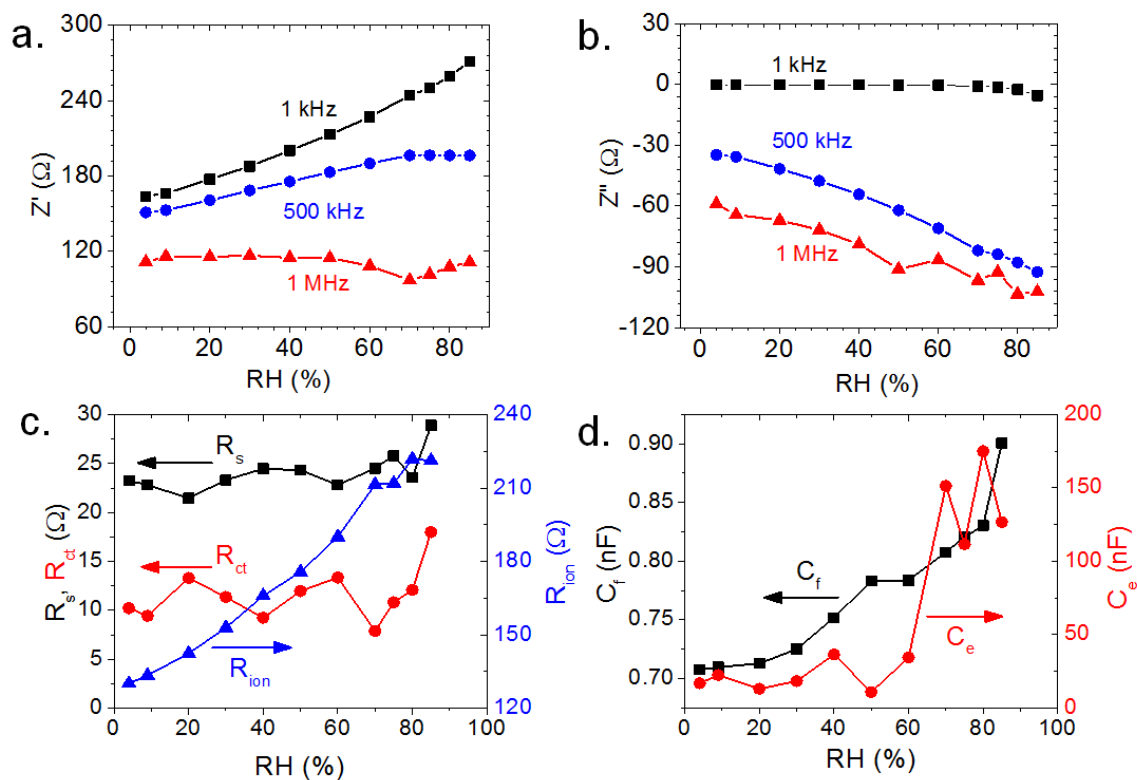


Figure 23. (a) Frequency-dependent real (Z') and (b) imaginary (Z'') impedance measured at 1 kHz, 500 kHz, and 1 MHz. (c) Equivalent circuit shunt resistance (R_s), ionic conduction resistance (R_{ion}), charge transfer resistance (R_{ct}), and (d) film capacitance (C_f) and film/electrode interface capacitance (C_e). Figure reproduced with permission.⁵⁶

increased, suggesting that the resistive RH response of PEDOT:PSS occurs primarily in the low frequency direct-current (DC) regime, which is consistent with ΔR reported in Figure 21(d). The value of Z'' shows weak ($|\Delta Z''| < 6 \Omega$) RH dependence at 1 kHz but exhibits strong RH response at higher frequencies, decreasing by over 100% at 500 kHz and by 70% at 1 MHz as RH is increased from 3% to 85%. The RH dependence of Z'' at high frequencies suggests that the change in Z'' is a consequence of the changing dielectric constant of the PEDOT:PSS film caused by inclusion of polarizable water molecules.

The derivatives of real impedance (dZ') and imaginary impedance (dZ'') at 1 kHz, 500 kHz, and 1 MHz were calculated to further investigate PEDOT:PSS electrical response to humidity. In general, the dZ' and dZ'' responses can be divided into at least three regions which resemble the regimes identified for large changes in ΔM and ΔR shown in Figure 21(d): $RH < 20\%$, $20\% < RH < 60\%$, and $RH > 60\%$. In most cases, dZ' and dZ'' change by 100% or more for $3\% < RH < 20\%$, which is likely associated with rapid adsorption of H_2O at hydrophilic HSO_3 surface sites. As RH approaches 20%, dZ' and dZ'' become relatively constant as low adsorption energy sites become saturated with water. Near 60% RH, a dramatic change in dZ' and dZ'' occurs, which likely corresponds to the same process responsible for changes in ΔM and ΔR at this RH level: saturation of the bulk film and formation of H_2O multilayers on the film surface.

RH dependence of equivalent circuit parameters is shown in Figure 23(c) and (d). Shunt resistance increases insignificantly (from 23-29 Ω) within the full measured RH range. Charge transfer resistance is not affected until $RH > 75\%$, likely due to condensation of water between domains at high RH. From 3% to 85% RH, ion conduction resistance increases by $\sim 70\%$ (from 130 Ω to 220 Ω). Evidence by Nardes et al. that ionic conduction channels begin contributing to conductivity of PEDOT:PSS at $RH > 30\%$ due to proton hopping between sulfonic acid groups¹⁸³ suggests that the increase in ionic conduction resistance

that we observe is due to a decrease in mobile ion concentration due to film swelling and formation of hydration spheres around mobile ions. We find that the interface capacitance and film capacitance increase significantly with RH. Capacitance at film/electrode interfaces exhibits a large increase at RH > 60%, likely as a result of water condensation which allows formation of metastable electrical double layer (EDL) structures comprised of hydronium ions (H_3O^+) and free hydrogen ions (H^+) generated by H_2O adsorption on hydrophilic PSS: $\text{H}_2\text{O} + \text{PSS}(\text{HSO}_3) \rightarrow \text{H}_3\text{O}^+\text{PSS}(\text{SO}_3)^-$.²⁰⁰ Film capacitance increases from 0.71 nF to 0.90 nF, which is closely related to the high dielectric constant of H_2O (~80) relative to the dielectric constant of PEDOT:PSS (~2-3)²⁰². It is likely that some of the observed increase in ion conduction resistance results from electric field screening of ions by polar water molecules.

Optical response to humidity

We explored changes in the optical properties of PEDOT:PSS film deposited on SiO_2 using variable-angle SPE under controlled RH conditions. SPE spectra measured at different RH levels were modeled in 450-1000 nm wavelength region to omit higher energy transitions of the spectrum which include Si/ SiO_2 contributions. A single layer of Tauc-Lorentz + Lorentz oscillators was used to model the PEDOT:PSS film. We evaluated the fit parameters for sensitivity (confidence limits) and correlations (two parameter correlation coefficients). The errors reported on the parameters were derived from $\text{FOM}_i = 1.65 \cdot \sqrt{C_{ii}} \cdot \sqrt{\text{MSE}}$ where MSE is the mean squared error and C_{ii} is a two-parameter correlation coefficient. The rates of change in direct and indirect optical bandgaps ($\Delta E_g/\Delta \text{RH}$) of the PEDOT:PSS film, as extracted from the SPE spectra, are shown in Figure 24. The values of $\Delta E_g/\Delta \text{RH}$ exhibit at least three different trends under changing RH conditions: the magnitude of $\Delta E_g/\Delta \text{RH}$ decreases by over 60% for $1\% < \text{RH} < 10\%$, remains roughly constant for $10\% < \text{RH} < 75\%$, and

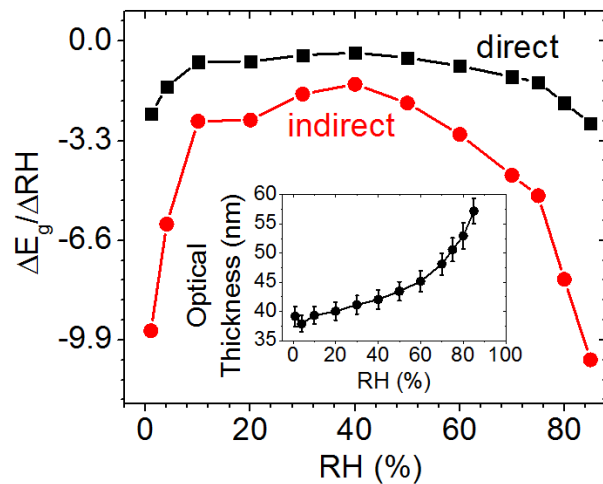


Figure 24. Rate of change in the optical bandgap (E_g) as estimated from spectroscopic ellipsometry. Units of $\Delta E_g/\Delta RH$ are in [eV/%]. Inset: optical thickness of PEDOT:PSS film as estimated from fit of SPE spectra. Error bars represent confidence limits estimated from MSE values of the fits. Figure reproduced with permission.⁵⁶

increases for $RH > 75\%$. These three regimes correspond to similar transitions observed in the ΔM , ΔR , and EIS data, which generally show a rapid change at low RH ($1\% < RH < 10-25\%$), stabilized change at intermediate RH ($10-25\% < RH < 60-75\%$), and increased change at high RH ($RH > 60-75\%$). This suggests that the same physical PEDOT:PSS-H₂O interactions are responsible for changes in rates of mass loading, conductivity, and optical (bandgap) responses. It is likely that the three regimes roughly correspond to rapid adsorption of H₂O at active sites at low RH, the slow adsorption and diffusion into the bulk film at mid-RH, and H₂O saturation and multilayer formation on the surface at high RH. Optical film thickness increases exponentially with RH (Figure 24 inset). Exponential swelling of the film is consistent with adsorption that resembles a type III BET isotherm²⁰³, suggesting that hydrogen bonding between gas-phase H₂O and adsorbed H₂O molecules leads to an increase in the rate of adsorption and film swelling as RH increases, which is consistent with previous observations of H₂O interaction with PEDOT:PSS film⁴⁰.

Wavelength-dependent real (ϵ_1) and imaginary (ϵ_2) dielectric constants, index of refraction (n), and extinction coefficient (k) of PEDOT:PSS at 1% and 85% RH were calculated. For $\lambda > 500$ nm, real dielectric constant/index of refraction increase with RH as H₂O loading of the PEDOT:PSS matrix increases polarizability of the film. RH dependence of the real dielectric constant/index of refraction is insignificant at $\lambda < 500$ nm due to low dispersion and optical extinction coefficient (< 0.05). The imaginary dielectric constant/extinction coefficient exhibit a bathochromic shift of ~ 75 nm as RH increases from 1% to 85%, indicating the creation of lower energy states. The peak shift corresponds to $\Delta E \approx 16$ eV which is likely related to the formation of EDLs comprised of H₃O⁺ and H⁺ ions between adjacent PEDOT:PSS domains. Formation of EDLs increases inter-domain capacitance and inhibits ion mobility³⁷, which is apparent from the large increases in R_{ion} and C_f shown in Figure 24. It is likely that the

formation of metastable EDLs also contributes to film swelling (Figure 24 inset) and the increased PEDOT:PSS surface potential at high RH.

To examine connections between electronic and optical responses of the PEDOT:PSS film under changing humidity, we extracted the real part of optical conductivity (σ_{op}) from the imaginary dielectric constant (ϵ_2) and optical frequency (ω) where $\sigma_{op} = \epsilon_2 \omega / 4\pi$. Wavelength-dependent optical conductivity of the film at different RH conditions is shown in Figure 25(a). As RH increases, optical conductivity decreases nonlinearly. The decrease in σ_{op} at $\lambda > 700$ nm is likely due to the high optical extinction coefficient of water at near infrared wavelengths. Since electrical conductivity is proportional to $1/R$, where R is the DC electrical resistance shown in Figure 21(d), it is possible to examine the RH dependence of optical and electrical conductivities together. To compare the PEDOT:PSS optical conductivity response to RH with electrical conductivity response to RH, we plotted σ_{op} as measured at $\lambda = 500$ nm with $1/R$ (Figure 25(b)). The values of σ_{op} and $1/R$ appear strongly correlated and exhibit behavior like that observed for the rate of change of optical band gap ($\Delta E_g / \Delta RH$) and the rate of mass loading ($\Delta M / \Delta RH$). Both electrical and optical conductivities decrease roughly exponentially as humidity is increased. Mobility of electronic charges decreases when swelling of the hydrophilic PSS matrix results in larger distances between adjacent conductive PEDOT domains. We speculate that film swelling along with the formation of EDL structures composed of H_3O^+ and H^+ ions results in reduced carrier mobility which concomitantly lowers electrical and optical conductivities in the film.

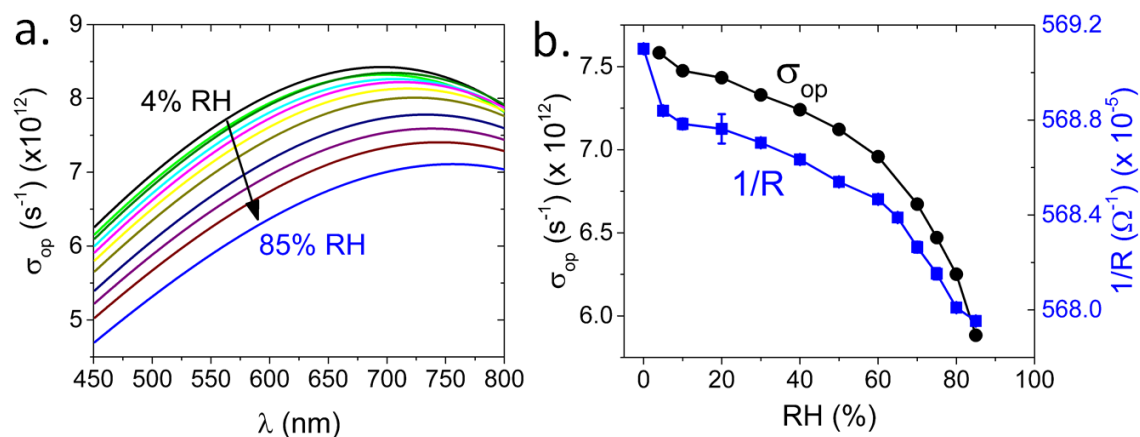


Figure 25. (a) Wavelength-dependent optical conductivity (σ_{op}) extracted from imaginary dielectric constant measured at different RH conditions. (b) Strong correlation between optical conductivity (extracted at 550 nm) and electrical conductivity, represented by inverse of DC resistance ($1/R$). Figure reproduced with permission.⁵⁶

Conclusions

We performed multimodal probing of the PEDOT:PSS-water interaction using nanoscale and mesoscale characterization to unfold connections between the electronic, ionic, optical, and structural humidity response of PEDOT:PSS films. We showed a direct correlation between decreases in electrical and optical conductivities as RH increases. Mass loading, DC electrical conductivity, optical conductivity, and optical bandgap changes in the film occurred in three primary RH regimes. Large changes occurred at low ($RH < 10\text{-}25\%$) and high ($RH > 60\text{-}75\%$) humidity conditions and small changes occurred at mid-RH conditions ($25\% < RH < 60\%$). The three regimes likely correspond to physical processes taking place in the film: rapid H_2O adsorption at active PSS sites at low RH, H_2O adsorption and diffusion throughout the bulk film at mid-RH, and H_2O saturation and multilayer formation on the film surface at high RH. As calculated from SPE spectra, optical film thickness swelled to 150% of its original thickness from 1% to 85% RH. Low frequency (1 kHz) impedance increased by $\sim 100\%$ and film capacitance increased by $\sim 30\%$ as RH was increased from 9% to 80%. Our results indicate that this was likely caused by a combination of film swelling, an increase in the average dielectric constant due to uptake of water, and formation of electrical double layers by mobile hydronium ions and protons. The results shed light on the correlation between nanoscale surface properties and mesoscale optoelectronic behavior of PEDOT:PSS under varying humidity conditions.

Chapter 7: Humidity response of ZnO-infiltrated SU-8

A version of this chapter was originally published By Eric Muckley, Liam Collins, Anton Ievlev, Xinyi Ye, Kim Kisslinger, Bobby Sumpter, Nikolay Lavrik, Chang-Yong Nam, and Ilia Ivanov:

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ToF-SIMS data was acquired by Anton Ievlev. Surface potential data was acquired by Liam Collins. TEM images were acquired by Chong-Yong Nam, Xinyi Ye, and Kim Kisslinger. This research was conducted at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory and Center for Functional Nanomaterials at Brookhaven National Laboratory (Contract No. DE-SC0012704), which are U.S. Department of Energy Office of Science User Facilities.

Abstract

Oxygen and water vapor sensing properties are investigated in metal-oxide–hybrid polymer nanocomposite thin films generated by infiltration synthesis, which incorporates molecular ZnO into the matrix of SU-8 polymer, a common negative-tone photoresist. The hybrid thin films display 20-fold higher gravimetric responses to oxygen and water vapor than those of control ZnO thin films in the dark. An additional 50–500% enhanced responses are detected under UV irradiation. The overall enhanced gravimetric response in the hybrid film is attributed to the ZnO molecules distributed in the polymer matrix, whereas the UV enhancement is explained by the light-induced, reversible generation of hydrophilic fluoroantimonic acid from triarylsulfonium hexafluoroantimonate

photoacids, which leads to the increased surface potential and adsorption energies for oxygen and water. A gravimetric sensor based on a series of ZnO-infiltrated SU-8 films under UV excitation enables 96% accurate classification of water and oxygen environment with sub 10 mTorr detection limits. The results demonstrate UV-induced fully reversible surface hydrophilicity of ZnO/SU-8 hybrid nanocomposites.

Introduction

The electrical and optical properties of ZnO, a wide and direct bandgap (~ 3.37 eV) semiconductor, lead to the development of sensors for water,^{63, 204} oxygen²⁰⁵, volatile organic compounds (VOCs)²⁰⁶⁻²⁰⁸, NO_x,²⁰⁹ ammonia²⁰⁸, and UV light⁶³.

Incorporation of ZnO nanoparticles in photolithographically patternable epoxy derivative of a bis-phenol-A Novolac (SU-8) leads to additional control of dielectric, elastic, or piezoelectric properties of polymer, while keeping composite compatible with complementary metal-oxide-semiconductor technology. ZnO-SU-8 composites showed Young modulus a factor of 4 higher than pure polymer²¹⁰⁻²¹¹ improving properties of low-cost piezoelectric microelectromechanical systems (MEMS) for applications in bio- and chemical sensing. SU-8 surface is not highly hydrophilic (static contact angle with water is about 80°), and for bio-MEMs applications SU-8 is usually UV-photo-grafted with 2-hydroxyethylmethacrylate or of poly-(ethylene glycol) hydrogels²¹² to make it hydrophilic. Exposure to oxygen plasma etching can also increase surface roughness and improve hydrophilicity of SU-8 (reducing contact angle to 30°).²¹³

Unlike SU-8, formation of highly hydrophilic (water contact angle smaller than 10°) surface of ZnO can be achieved under UV irradiation. This photo-wetting of

ZnO is reversible, and it was successfully incorporated in a design of functional surfaces.^{63, 214-215} Photo-switchable wetting was also reported for a micro–nanostructure-layered system composed of TiO₂ nanorod-coated SU-8 micropillars, where TiO₂ enables photo-switching behavior and SU-8 serves as passive macrostructural element.²¹⁶ No evidence that UV irradiation could affect contact angle of polymer without TiO₂ was reported.

We speculate that residual of photo-acid generator (PAG), such as triarylsulfonium hexafluoroantimonate ((Ar)₃S⁺SbF₆[−]), used for crosslinking SU-8 monomers and left in polymer after crosslinking, could lead to photo-wetting behavior, and thus enhanced sensing. UV light exposure could decompose the PAG to H⁺SbF₆[−] which acts as a catalyst for cationic polymerization by opening SU-8 epoxy rings during thermal annealing, resulting in a chemically-stable crosslinked SU-8 matrix²¹⁷⁻²¹⁹. H⁺SbF₆[−] is strongly hydrophilic and forms fluoroantimonic acid hexahydrate (H⁺SbF₆[−] + 6H₂O) upon exposure to water²²⁰, but its reactivity as a superacid prevents utilization of H⁺SbF₆[−] for common H₂O-sensing applications.

To incorporate different concentrations of ZnO nanoparticles in SU-8 polymer film, atomic layer deposition (ALD) was used. ALD offers a low temperature alternative to conventional ZnO synthesis techniques which require high temperatures (340–500°C)^{208, 221} incompatible with polymer films. ALD also enables increased concentration of ZnO nanoparticles in the film by increasing number of deposition cycles, which is difficult to achieve for ZnO nanoparticle/SU-8 monomer mixtures, due to strong UV adsorption and scattering properties of ZnO. While ALD-synthesized ZnO/SU-8 composites have already been reported, no reliable information is given about the distribution of ZnO in nanometer-thin film, which is critical to explain the mechanism of sensing and mechanical properties of ZnO/SU-8 composites. This unsolved question is

addressed here by analysis of the distribution of ZnO in ZnO/SU-8 composite as a function of ZnO infiltration cycles.

The gravimetric response of ZnO-infiltrated SU-8 thin films deposited on a quartz crystal microbalance (QCM) to relative humidity (RH) and oxygen in the dark and under UV irradiation was investigated. The QCM is a thickness-shear mode resonator which is used for a broad range of environmental sensing applications due to its sub-nanogram sensitivity and compatibility with gas, liquid, and vacuum environments^{33, 37, 58, 62}. Measurement of the dynamic frequency response of QCM coated with nanometer-thin polymer or oxide films allows *in situ* monitoring of analyte sorption kinetics^{40, 56} and provides a platform for testing effects of UV activation on gravimetric response of adsorbent films⁵⁸⁻⁵⁹. Integration of basic ZnO oxide nanoparticles in SU-8 matrix is expected to increase surface area and either passivate super acid or enhance interaction with water due to photo-wetting of ZnO²²²⁻²²⁵.

Hybrid nanocomposite prepared by ALD infiltration synthesis of molecular ZnO in SU-8 thin films exhibits a significantly enhanced gravimetric response to water vapor and oxygen compared with a control samples of pure SU-8 or ZnO thin film. Further enhancement of sensor response is realized by exposing films to UV irradiation. Through the complementary structural, physical, and chemical analyses the enhanced gas sensing functionality is explained by mechanism of the increased number of adsorption sites originating from the infiltrated ZnO, which leads to reversible formation of fluoroantimonic acid and subsequent enhancement of composite's affinity for oxygen and water molecules. The results demonstrate a new sensing functionality realized by infiltration synthesis and reveal a sensing mechanism based on reversible UV-induced chemical changes, which may enable enhanced control of the gas/vapor sensor selectivity and sensitivity.

Experiment

Commercially available SU-8 2002 solutions (MicroChem) diluted in cyclopentanone (SigmaAldrich) were used for experiments. The diluted SU-8 solution was spin-cast at 2000 rpm for 45 s to prepare ~100 nm thick SU-8 films on precleaned 5 MHz AT-cut Au-coated QCM crystals, SiO₂/Si substrates with prepatterned 2 μ m spaced interdigitated electrodes, and bare Si substrates. The spin-cast films were subjected to the ambient pre-cross-linking baking for 1 min at 65 °C and additional 3 min at 95 °C on a hot plate (i.e., soft bake). The samples were then exposed to UV light for 5 min under nitrogen using a UV light chamber equipped with a low-pressure Hg lamp (American Ultraviolet Co.), followed by the postexposure bake for 2 min at 95 °C in ambient air to complete the cross-linking. The film thickness was measured by an interferometer (Filmetrics).

The ZnO-infiltration synthesis was performed on the spin-cast SU-8 thin films at 85°C in a commercial ALD system (Cambridge Nanotech Savannah S100) using the procedure described in our previous report.²²⁵ Diethylzinc, DEZ (Aldrich), and water were used as the organometallic Zn precursor and oxidant. Each ZnO-infiltration synthesis cycle consists of (a) exposure of SU-8 films to DEZ for 300 s under the static vacuum (chamber pressure ~ 2 Torr); (b) purge of the reactor by 100 sccm N₂ flow for 60 s; (c) exposure of SU-8 films to water vapor for 300 s under the static vacuum (pressure ~ 10 Torr); and (d) purge of the reactor by 100 sccm N₂ for 300 s. 4–16 cycles of ZnO infiltration to the samples. Control ALD-mode ZnO thin films were prepared by simply placing bare inorganic substrates (e.g., Au-coated QCM crystals) with no SU-8 film coating during the infiltration synthesis on “hard” inorganic substrates, the precursors cannot diffuse into the substrates, only allowing the typical, surface-limited normal ALD with a deposition rate of ~1 Å/cycle.²²⁴⁻²²⁵

SU-8 thin film was examined after 10 cycles of ZnO-infiltration synthesis by cross-sectional TEM (JEOL 1400, 120 kV). The cross-sectional TEM sample was prepared by the lift-out technique in a focused ion beam system (FEI Helios) using evaporated carbon and top Au protective layers applied on top of the sample.

All atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) measurements were performed on a commercial AFM (Cypher, Asylum Research and Oxford instr. Company), using as-received Pt/Ir-coated AFM probes (Nanosensors, PPP-EFM), with a nominal mechanical resonance frequency and spring constant of 75 kHz and 2.8 N/m, respectively. Measurements were performed using amplitude modulated detection in lift mode, or two pass modes, with the lift height being between 50 and 100 nm ensuring the response was purely electrostatic in nature

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed in positive ion detection mode using a TOF-SIMS-NSC (ION-TOF GmbH) instrument inside an ultrahigh vacuum chamber at $\sim 6.4 \times 10^{-6}$ Torr. Liquid metal Bi³⁺ ion gun (30 keV energy, 30 nA current) was used as a primary source with a focused ion beam spot size of $\sim 5 \mu\text{m}$, and mass resolution $m/\Delta m \sim 5000$. Cs⁺ ion beam with energy of 1 keV and current 70 nA was used for depth profiling with spot size $\sim 20 \mu\text{m}$. Sputter crater size was 300 μm . Measurements were done in non-inter-laced mode, when every scan by the bismuth ion beam was followed by a 1 s sputtering cycle. Cs₂OH⁺ and Cs₂F⁺ clusters were used to detect spatial distribution of negative ions of OH⁻ and F⁻, respectively

For Raman spectroscopy, ZnO-infiltrated hybrid SU-8 films on SiO₂/Si substrates were characterized in 100–7500 cm⁻¹ frequency range using inVia Qontor confocal Raman spectrometer (Renishaw equipped with 300 l/mm grating).

Raman and fluorescence spectra of thin films were measured in backscattering geometry through a 20× objective using 633 nm laser operated at 5 mW. The final spectrum is an average of seven spectra taken at different locations on the sample.

The contact angles of deionized water on the ZnO-infiltrated hybrid SU-8 films with varying numbers of infiltration synthesis cycles were measured by a KRÜ SS DSA 30 contact angle goniometer in the dark and under UV irradiation produced by an Hg lamp (254 nm) placed 5 cm away from the film surface.

All electrical and gravimetric measurements were performed at 27 ± 0.5 °C inside a modified controlled environmental chamber (Surface Measurement Systems). Prior to gas/vapor adsorption measurements, films were placed under 10^{-5} Torr (1.33×10^{-5} mbar) vacuum for 12 hours. QCM frequency shift was recorded using a commercial QCM system (SRS QCM200). Gas/vapor pressure was controlled by injecting O₂/H₂O into the vacuum chamber using a mass flow controller at 20 cm³/min flow rate. A LabVIEW program was used to control gas/vapor flow and record frequency shift of the QCM during the experiment. An Hg pen lamp was mounted outside the vacuum chamber through a quartz window for UV irradiation experiments. The spectral irradiance of UV lamp was measured by an optical power meter (Newport 2931-C with 918D UV detector head). Direct-current (DC) electrical resistance measurements were performed with a source-measure unit (Keithley 2420).

Results and discussion

Microstructure and chemical depth profiling

The cross-sectional TEM examined the microstructure of 10-cycle ZnO-infiltrated SU-8 film, confirming the infiltration of molecular ZnO within the matrix SU-8 film. The high-contrast bright-field cross-sectional TEM image (Figure 26(a) left panel) features a dark contrast in the 40 – 50 nm depth of the upper portion of SU-8 film, originating from the high atomic number of Zn in the ZnO-infiltrated polymer matrix. A higher magnification image (Figure 26(a) right panel) further reveals the infiltrated ZnO does not form any visible crystallinity or aggregation in the polymer matrix while resulting in a 4 – 5 nm thick dense layer atop the film. The observed infiltration depth, amorphous nature of the ZnO-infiltrated hybrid, and dense top layer are all consistent with our earlier study⁶³. The cross-sectional TEM images indicate a seemingly smooth surface in the given field of view and the AFM examination of the top surface reveals some sporadic small spheroidal domains of 5 – 20 nm radius on the film surface, but otherwise a background with a roughness comparable to that of the control ZnO film simultaneously formed on a separate substrate without the SU-8 coating during the infiltration synthesis (root-mean-square roughness <1 nm).

Chemical depth profiles of SU-8 film after 0, 4, 8 and 16 cycles of ZnO infiltration synthesis were further investigated using ToF-SIMS. Figure 26(b) shows the average chemical depth profiles for SU-8 films with 4, 8 and 16 ZnO infiltration cycles with standard deviation represented by error bars. Sputter time corresponds to film depth, where the time value of 0 s corresponds to the hybrid film surface. The intensity of the Si⁺ peak suggests that the SiO₂/Si substrate surface was reached after 150 – 200 s of sputtering. Peaks attributed to Cs₂F⁺, Cs₂OH⁺ and C₂H₅⁺ were observed throughout the film. The presence of fluoride

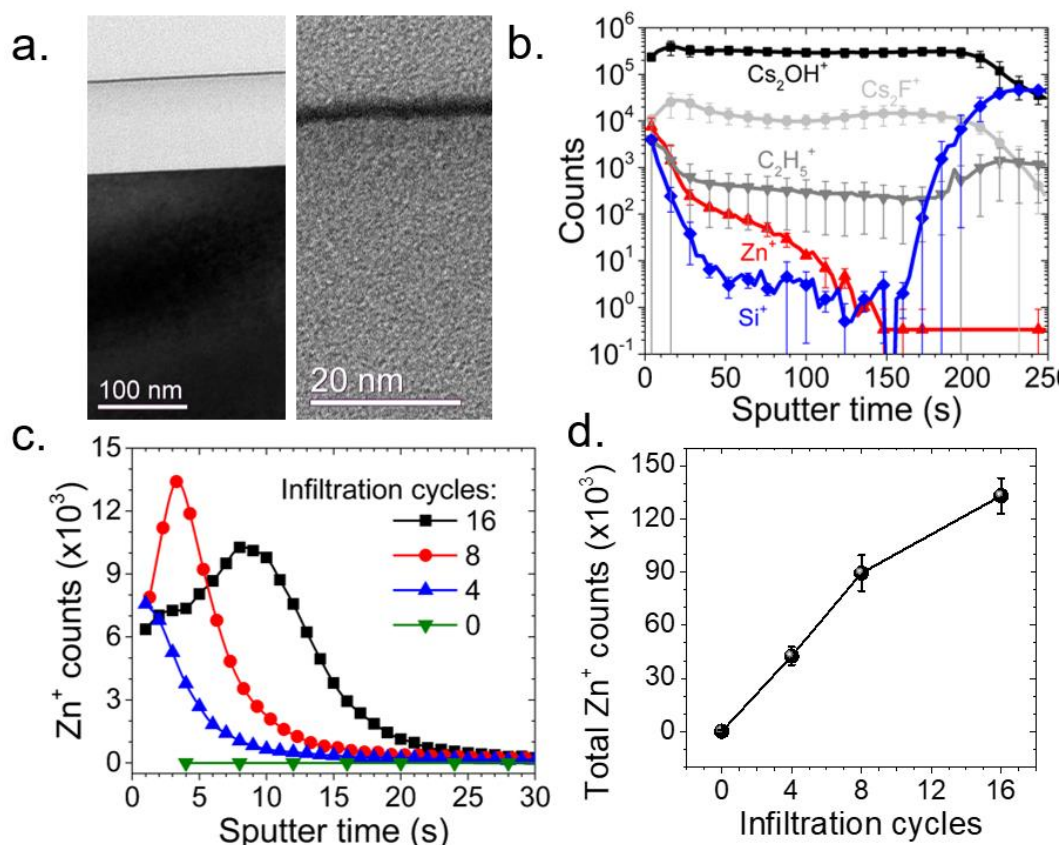


Figure 26. (a) Cross-sectional bright-field TEM images of SU-8 film after 10 cycles of ZnO-infiltration synthesis, with the left panel showing a low-magnification, high-contrast view of the whole hybrid film and the right panel the upper portion of the film including the top dense layer at a higher magnification. (b) Intensity of ToF-SIMS peaks attributed to Cs_2OH^+ , Cs_2F^+ , C_2H_5^+ , Zn^+ , and Si^+ measured as a function of sputter time. Error bars represent the standard deviation between four different films. Sputter time is correlated to film depth, where 0 s corresponds to the film surface. (c) Profile of ToF-SIMS peak attributed to Zn^+ in films with 0, 4, 8, and 16 infiltration cycles. (d) Total Zn^+ counts, which is directly proportional to concentration of Zn in films, with 0, 4, 8, and 16 infiltration cycles. Figure reproduced with permission.²²⁶

can be attributed to the PAG which is uniformly distributed through the film thickness. The presence of C_2H_5^+ ions with heightened intensity near the surface was detected, most likely due to the terminal ethyl group of ZnO precursor, diethylzinc (DEZ), resulting from its incomplete reaction with water (i.e., $\text{C}_2\text{H}_5\text{-Zn-C}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{-Zn-OH} + \text{C}_2\text{H}_6$), or the reaction byproduct C_2H_6 .²²⁴⁻²²⁵ The presence of Cs_2OH^+ throughout the whole film thickness indicates an abundance of hydroxyl terminations within the film, which can originate from both the crosslinking reaction of epoxy groups in SU-8 during the initial film preparation and the reaction between DEZ and water during the infiltration synthesis.²²⁰ Given the largely constant depth profile of Cs_2OH , the former is the more likely cause of the presence of hydroxyl groups, which in fact can serve as adsorption sites for H_2O and O_2 adsorbates. The highest concentration of Zn^+ was detected near the film surface, corresponding to the 4 – 5 nm thick dense layer observed in the cross-sectional TEM. The dense layer is attributed to the repeating infiltration synthesis cycles that start blocking pores in the polymer matrix, limiting the continued diffusion of material precursors down into the bulk film. To examine the effect of the number of infiltration cycles on the depth profile of infiltrated ZnO in SU-8, Zn^+ distributions are shown in Figure 26(c). SU-8 film with 0 ZnO infiltration cycle served as a reference. As the number of infiltration cycles increased, the infiltrated ZnO appears distributed more from the surface to the interior of SU-8 thin film. Zn^+ concentration decreased sharply after ~20 s of sputtering, suggesting that the highly ZnO-rich region extended from the surface down to ~15% of the film thickness depth. The area under the Zn^+ peak was used to estimate the total abundance of infiltrated ZnO in the film (Figure 26(d)). Zn^+ peak area increased roughly linearly with the number of infiltration cycles. A consistent, linear increase of the amount of infiltrated ZnO within the SU-8 film with increasing number of infiltration cycles has been previously observed by *in situ* mass gain measurements, which identified the mass gain of $0.68 \mu\text{g}/\text{cm}^2$ per infiltration cycle, equivalent to the ZnO thickness of $\sim 10.2 \text{ \AA}$ per cycle (assuming the density of ZnO is $5.61 \text{ g}/\text{cm}^3$), a more than 10-fold larger deposition rate than

that of the normal ALD process, highlighting the distinct deposition mode of infiltration synthesis.²²⁵

Gravimetric gas-sensing properties

To investigate the effect of ZnO infiltration on gas sensing properties of SU-8 films, the hybrid films prepared on QCM crystals were exposed to controlled pressure pulses of oxygen and water vapor at room temperature in the dark. Control ZnO films deposited by ALD mode on polished gold-coated QCM crystals without SU-8 templates exhibited low gravimetric response (~ 1 Hz/cm², corresponding to ~ 20 ng/cm² under Sauerbrey conditions³⁶) during exposure to 22.6 Torr pulses of O₂ and H₂O vapor. The response of ZnO films was similar to that of bare gold reference crystals, which indicates a lack of selective H₂O and O₂ adsorption on ZnO likely due to the low surface area and lack of reactive ZnO terminations (e.g., unhydroxylated ZnO(1010) lattice planes containing O or Zn vacancies)⁶³ resulting from the deposition of ZnO under the normal ALD mode. Frequency shift was roughly linear with gas/vapor pressure, for the partial pressure range from 0.24 Torr ($\sim 1\%$ RH) to 22.6 Torr ($\sim 95\%$ RH)²²⁶, consistent with findings of Zhang et al. who reported the linear gravimetric RH response from ZnO nanowire/nanorod-coated QCM crystals in the 5–97% RH range.²²⁷ We note that although the UV activation was previously reported to enhance ZnO gas/vapor response,²²⁸ the effects of UV were not investigated on the control ALD-deposited ZnO films due to the lack of selective H₂O and O₂ adsorption.

In contrast to the control ZnO film, the ZnO-infiltrated hybrid SU-8 exhibited remarkably enhanced gravimetric sensing responses to H₂O and O₂, which was further increased under UV irradiation. ZnO-infiltrated SU-8 films featured up to a factor of 20 higher gravimetric response (~ 20 Hz/cm²) to H₂O and O₂ than the control ZnO films on bare QCM crystals²²⁶. Considering that the insignificant

difference in surface roughness between the ZnO-infiltrated SU-8 hybrid and control ZnO films, the order of magnitude higher gravimetric responses was ascribed to higher analyte accessibility to active ZnO sites within the bulk of ZnO-infiltrated hybrid film, along with the presence of additional adsorption sites associated with hydroxyl groups in the SU-8 matrix.

More detailed gravimetric response characteristics of ZnO-infiltrated SU-8 films are found in the normalized temporal frequency shift measured during exposure to 22.6 Torr pulses of HO (corresponding to ~95% RH) and O₂ under continuous UV irradiation and in the dark (Figure 27(a) and (b)). Frequency shifts and response times (corresponding to the exponential decay constant to be discussed later) generally increased by a factor of 2 or more during UV irradiation, particularly during O₂ exposure most likely due to the photoactivation of O₂ adsorption sites on ZnO.⁶³ Exposure to UV irradiation increased gravimetric response of ZnO-infiltrated films to O₂ by a factor of 5 compared with its response to oxygen in dark. Density functional theory (DFT) calculations that included self-consistent van der Waals corrections also indicated a substantial increase in the interaction of a water molecule with fluoroantimonic acid, ~0.36 eV over triarylsulfonium hexafluoroantimonate. Additionally, a hydration shell of six water molecules was found to be easily supported by fluoroantimonic acid, corroborating the experimental results for the UV effect and the hypothesized mechanism. The infiltration-cycle-dependent frequency shift in response to 22.6 Torr gas/vapor pulses (Figure 27(c)) further shows that the gas/vapor response of the hybrid film increased with increasing number of ZnO-infiltration cycles from 0 to 8, likely resulting from an increase in the number of gas/vapor adsorption sites associated with molecular ZnO imbedded within the SU-8 matrix, such as hydroxyl groups and oxygen vacancies.^{63, 204, 229-230} The SU-8 film with 16 ZnO-infiltration synthesis cycles showed smaller gas/vapor response than the film, which underwent 8 infiltration cycles, which suggests that repeated infiltration cycling and subsequent ZnO accumulation in the top dense layer of hybrid film

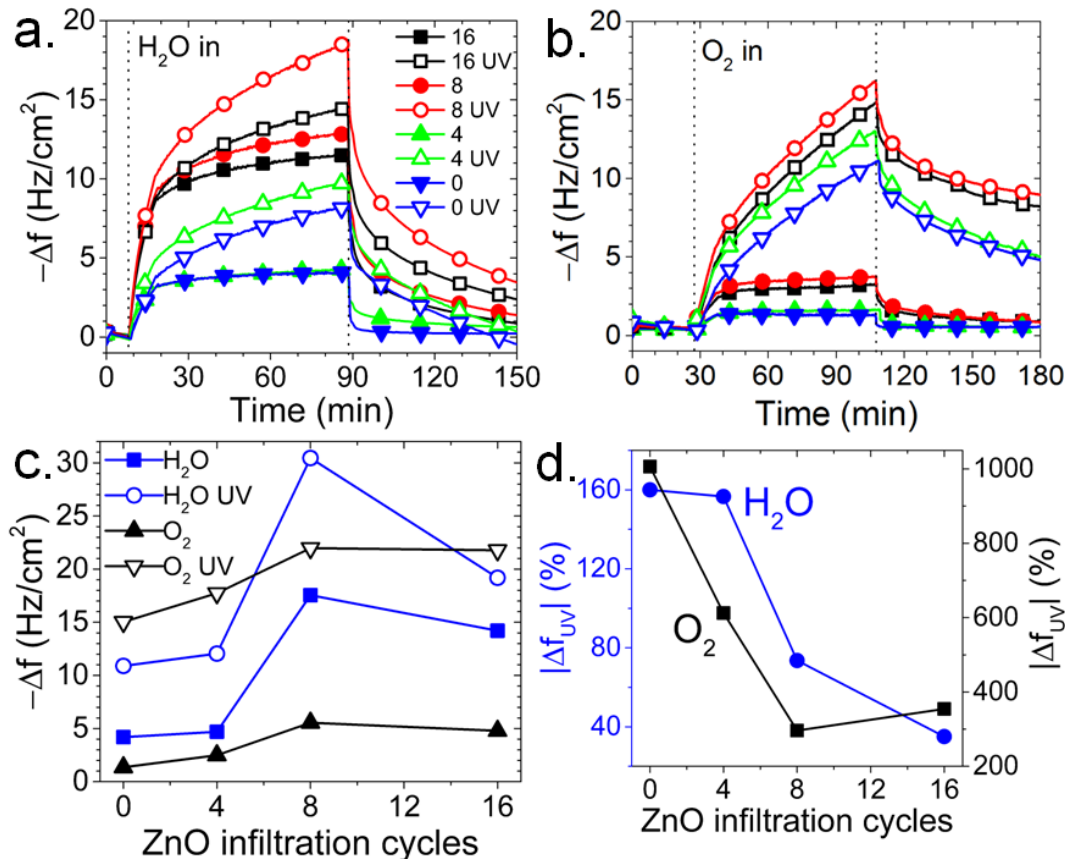


Figure 27. Normalized temporal frequency shift (Δf) of ZnO-infiltrated SU-8 films during exposure to (a) 22.6 Torr ($\sim 95\%$ RH) pulse of H₂O vapor and (b) 22.6 Torr pulse of O₂. The data are normalized to $\Delta f = 0$ Hz at time = 0 s. Gas/vapor exposure and removal are marked by the vertical dotted lines. Numbers in legend correspond to number of ZnO-infiltration cycles and whether response was measured in the dark or under UV irradiation. (c) Frequency shift vs number of ZnO-infiltration cycles during exposure to H₂O and O₂ in the dark and under UV irradiation. Magnitudes shown in (c) are slightly higher than those in (a) and (b) because they were extracted from the absolute frequency shift²²⁶. (d) Percent change in frequency shift ($|\Delta f_{UV}|$) between films exposed to gas/vapor in the dark and those measured under UV irradiation. Left and right axes show differences in frequency shift when films were UV irradiated during exposure to H₂O vapor and O₂, respectively. Figure reproduced with permission.²²⁶

eventually restricts analyte diffusion into the ZnO/polymer network. Un-infiltrated control SU-8 films exhibited only $\sim 4 \text{ Hz/cm}^2$ frequency shift ($\sim 70 \text{ ng/cm}^2$ under Sauerbrey conditions) during exposure to water, comparable to the previously reported value for SU-8, but ~ 5 -fold lower than that of the ZnO-infiltrated hybrid film, thus showing that the infiltrated ZnO within SU-8 matrix plays a critical role in enhancing the gravimetric response of ZnO-infiltrated SU-8 hybrid film to gas/vapor. It is noted that water vapor is known to exhibit Fickian diffusion and relatively low adsorption in pure SU-8 thin film.²³¹

Origins of UV-activated gas sensing

The effect of UV irradiation was further investigated and correlated with the presence of PAG in the SU-8 matrix and the UV-blocking properties of ZnO. To examine the effect of ZnO infiltration on UV enhancement of gravimetric response, the percent change in frequency shift due to UV irradiation ($|\Delta f_{UV}|$) is shown in Figure 27(d). During both H_2O and O_2 exposures, the effect of UV light decreased with increasing number of ZnO-infiltration cycles, suggesting that the UV enhancement of gravimetric response is originating from the infiltrated film bulk as the highly ZnO-concentrated, top dense layer in the hybrid film can act as an effective UV-blocking layer protecting the underlying polymer.²³² The notion is further supported by the fact that the ZnO thin film itself has been shown to have a UV-enhanced $\text{H}_2\text{O}/\text{O}_2$ adsorption^{63, 229} with increasing number of ZnO-infiltration cycles, the top dense layer on hybrid film is becoming more ZnO concentrated, but the UV enhancement was decreasing.

We suspect the most likely chemical entity in the bulk of hybrid film that can induce the observed UV-activated adsorptions of H_2O and O_2 is the decomposition/activation of residual PAG in the SU-8 matrix into H^+SbF_6^- , which can form fluoroantimonic acid hexahydrate ($\text{H}^+\text{SbF}_6^- + 6\text{H}_2\text{O}$) upon exposure to

water.²²⁰ Our previous study did show the presence of residual PAGs in the ZnO-infiltrated SU-8.²²⁴⁻²²⁵ Considering that the light-induced activation of H^+SbF_6^- should affect the surface energy, H_2O contact angle measurements were performed on the ZnO-infiltrated SU-8 hybrid film in the dark and under UV irradiation (Figure 28(a))²²⁶. The contact angle in the ALD-mode-deposited ZnO reference film decreased by $\sim 19^\circ$ upon exposure to UV irradiation (not shown), whereas that in the ZnO-infiltrated SU-8 film decreased by an average of $\sim 10^\circ$ upon exposure to UV irradiation. We infer that the UV response in un-infiltrated film is likely related to the presence of PAG in the SU-8 matrix, which reversibly decomposes to hydrophilic H^+SbF_6^- , increasing the affinity of ZnO-infiltrated SU-8 hybrid films to water and oxygen. The onium salt PAG in SU-8, $(\text{Ar})_3\text{S}^+\text{SbF}_6^-$, generally decomposes to acidic H^+SbF_6^- by UV irradiation, catalyzing the SU-8 polymerization under thermal baking.²¹⁹ Fluorine detected throughout the whole thickness of ZnO-infiltrated SU-8 hybrid film by ToF-SIMS (Figure 26(b)) confirms that PAGs are present in abundance at the surface and interior of the SU-8 film after ZnO-infiltration synthesis. We note that the UV-induced superhydrophobic to superhydrophilic transition in ZnO thin films has been attributed to the photodesorption of oxygen previously, which results in hydrophilic hydroxyl terminations.²³⁰ This can be one factor underlying the UV-enhanced hydrophilicity observed in ZnO-infiltrated films, but does not explain the increased hydrophilicity in un-infiltrated control SU-8 films.

The UV-induced changes in the surface energies of control ZnO and ZnO-infiltrated SU-8 hybrid films in the dark and under UV irradiation were further probed using KPFM (Figure 28(b))²²⁶. UV irradiation resulted in a $\sim 16\%$ increase in contact potential difference (VCPD) in ZnO film and a $\sim 12\%$ increase in surface potential of ZnO-infiltrated hybrid SU-8 film. The value observed from the control ZnO film is in agreement with UV-induced VCPD increase reported in ZnO nanowires via the photodesorption of oxygen from the ZnO surface.²⁰⁵ VCPD in ZnO consists of roughly Gaussian distribution of potentials, which

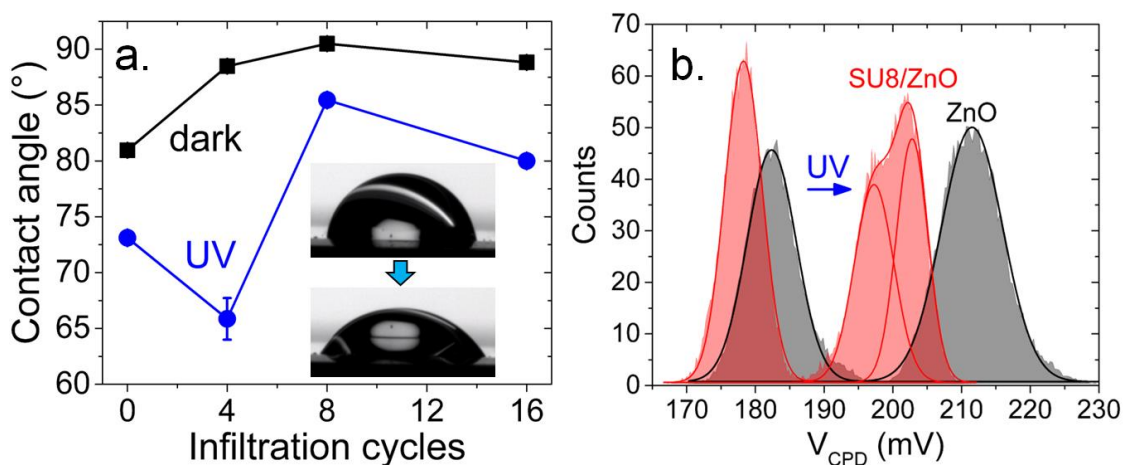


Figure 28. (a) Contact angle of water droplet measured on SU-8 films with 0, 4, 8, and 16 ZnO-infiltration cycles in the dark and under UV irradiation. Inset shows representative images of droplets in the dark (top) and under UV irradiation (bottom). Contact angles were measured after 2 min of droplet formation. (b) Histograms of contact potential difference (V_{CPD}) measured using KPFM in the dark and under UV irradiation for eight cycle ZnO (black) and eight cycle ZnO-infiltrated SU-8 (red). Figure reproduced with permission.²²⁶

undergoes a ~30 mV energy shift upon UV irradiation (black curves in Figure 28(b)). In the ZnO-infiltrated SU-8 film, the UV irradiation results in splitting of the single Gaussian VCPD distribution into at least two distinct levels, which are shifted by ~19 and ~25 mV (red curves in Figure 28(b)). One of the peaks likely corresponds to energies associated with UV-activated ZnO. The other peak is not present in the ZnO film and must be associated with the SU-8 matrix, but only appears during UV irradiation. This suggests that it is related to ionic byproducts of $(\text{Ar})_3\text{S}^+\text{SbF}_6^-$, which reversibly decomposes each time the film is exposed to UV irradiation.

Investigation of O₂ and H₂O adsorption

To further study gas/vapor adsorption on ZnO-infiltrated SU-8 hybrid films, the magnitudes of frequency shifts after 80 min of exposure to H₂O and O₂ pulses are plotted against gas/vapor pressure (Figure 29(a)). The gravimetric responses to gas/vapor pressure closely resemble modified Toth isotherms, shown fitted to experimental data by the solid lines ($r^2 > 0.98$ for each fit, where r is the residual in data fitting). Data were fitted by nonlinear least squares optimization using the SciPy library in Python.²³³ Other common isotherms, including Langmuir, Temkin, and Freundlich models, were fitted and resulted in less suitable fits (average $r^2 \leq 0.9$). The Toth isotherm is an empirical Langmuir-type model modified for heterogeneous adsorption on rough surfaces that yields an asymmetrical distribution of adsorption energies.²³⁴ The Toth model is used for describing a broad range of interactions because of its predictive behavior from low (Henry-type limit) to high (saturation limit) pressures²³⁵ and its suitability for systems limited to submonolayer coverage.²³⁶ A modified Toth isotherm can be represented by

$$M = \frac{K_T p_R}{[1 + (K_T p_R)^t]^{1/t}} , \quad (1)$$

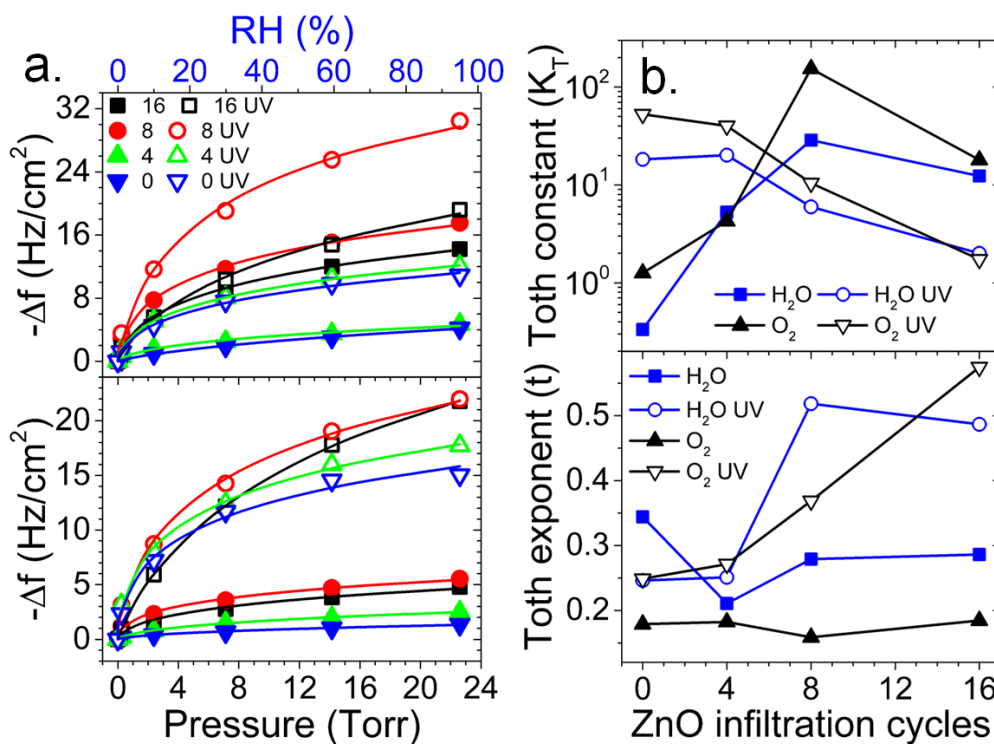


Figure 29. (a) Frequency shifts of ZnO-infiltrated SU-8 films after 80 min of H_2O (top panel) and O_2 exposures (bottom panel) at different gas/vapor pressures and illumination conditions (dark or UV). RH corresponding to each H_2O vapor pressure is shown on top horizontal axis. The solid lines correspond to fits to the Toth isotherm. Error bars correspond to noise signal in frequency shift measurements. (b) Corresponding Toth isotherm constants (K_T , top panel) and Toth exponents (t , bottom panel) extracted from Toth isotherm fits in (a). Note the use of logarithmic scale in top panel. Error bars correspond to uncertainties propagated from noise signal in frequency shift measurements. Figure reproduced with permission.²²⁶

where fitting parameters K_T and t are the Toth isotherm constant and Toth exponent, respectively. Total adsorbate mass (M) and relative analyte pressure (p_R) were normalized prior to fitting to produce unitless K_T and t parameters. Total adsorbate mass was calculated by converting frequency shift to mass using the Sauerbrey equation and normalized by $M = \Delta M/M_0$, where ΔM is the measured mass change shown in Figure 29(a), and M_0 is the maximum mass change which occurred in each film at the highest analyte pressure (22.6 Torr). Relative analyte pressure was defined as $p_R = p/p_0$, where p is the analyte partial pressure and p_0 is the partial pressure of H_2O at saturation at 27°C ($p_0 \approx 23.8$ Torr). The Toth isotherm constant K_T corresponds to the adsorption affinity of a specific adsorbent–adsorbate pair and is related to its average adsorption energy. The Toth exponent t corresponds to homogeneity of the adsorbent surface, where $0 < t \leq 1$. For example, a completely homogeneous surface has $t = 1$, and the corresponding Toth isotherm reduces to the well-known Langmuir equation.²³⁷ To investigate effects of ZnO-infiltration synthesis on the adsorption affinity and heterogeneity of SU-8 films, the values of K_T and t were extracted from the Toth isotherm fits. Un-infiltrated SU-8 films exhibited a high adsorption affinity (K_T) under UV irradiation, likely due to photoactivation of hydrophilic $H^+SbF_6^-$ as discussed (Figure 29(b), top panel). K_T decreased by roughly an order of magnitude as the number of ZnO-infiltration cycles increased, which likely occurs as UV is being blocked by the dense layer of ZnO accumulated near the film surface. In the dark, K_T was enhanced by increasing the number of ZnO-infiltration cycles (up to eight) due to the increase in available active adsorption sites associated with infiltrated ZnO. For the film with 16 ZnO-infiltration cycles, the ZnO accumulation near the surface likely blocks pores and prevents diffusion of analytes into the bulk film, thus reducing the average K_T .

The Toth exponent t , corresponding to film homogeneity, did not show a strong dependence on the number of ZnO-infiltration synthesis cycles when adsorption occurred in the dark (Figure 29(b), bottom panel). This is expected since the

majority of gas/vapor adsorption was associated with the photoactivated H^+SbF_6^- . In the dark, the value of t is generally larger for H_2O adsorption than for O_2 adsorption, indicating greater heterogeneity in O_2 adsorption sites than those of H_2O . This suggests that H_2O adsorption in the dark is primarily mediated by physical dipole and van der Waals interactions, for example between H_2O and hydroxyl groups or previously adsorbed H_2O molecules.²⁰⁴ Meanwhile, O_2 adsorption may be associated with a range of different adsorption energies including those corresponding to the dissociative chemical adsorption at oxygen vacancies on the ZnO surface. Under UV irradiation, t increases by a factor of ~ 2 as the infiltration synthesis increased from 0 to 16 cycles. Homogenization of the adsorption surface in the hybrid matrix is expected to occur as the SU-8 matrix is infused with the infiltrating molecular ZnO, and the hydrophilic fluoroantimonic becomes inaccessible to adsorbate molecules. The homogenization of adsorption sites on ZnO can also occur because the photodesorption of oxygen is known to result in hydrophilic hydroxyl terminations on ZnO surface.²³⁰ It is noted that the Toth isotherm adsorption behavior observed in ZnO-infiltrated SU-8 films stands in contrast to the linear frequency shift observed in control ALD-mode ZnO films prepared on bare Au-coated QCM crystals²²⁶ as well as the linear response observed by Zhang et al. from the ZnO nanowire/nanorod-coated QCM crystals in the 5–97% RH range.²²⁷ This provides further evidence that the nonlinear gas/vapor gravimetric response of ZnO-infiltrated SU-8 hybrid films can be attributed primarily to the presence of adsorption sites associated with SU-8.

Performance of gravimetric vapor sensing

To assess the performance of ZnO-infiltrated hybrid SU-8 films as adsorbent materials for gas/vapor sensors, detection limits were estimated from the signal-to-noise ratio and magnitude of QCM response. Minimum detection limits for both O_2 and H_2O vapor generally decreased by an order of magnitude or more when

the ZnO-infiltration synthesis was applied to SU-8 thin films, highlighting the enhanced sensing performance enabled by more available adsorption sites in the hybrid film. The limits further decreased by a factor of ~ 2 under UV irradiation, driven by the activation of hydrophilic fluoroantimonic acid and photodesorption of oxygen from ZnO-adsorption sites, as discussed previously.⁶³ Under UV irradiation, SU-8 film with eight ZnO-infiltration synthesis cycles achieved the lowest detection limits corresponding to ~ 0.004 Torr O₂ and $\sim 0.02\%$ RH and showed potential for wide-range humidity sensing from 1 to 95% RH. The ZnO-infiltrated hybrid SU-8 film enabled significantly enhanced RH sensitivity (bottom panel) under a broad humidity range compared with the reported performances of other metal oxides (sensitive to 2% RH in 5–99% RH range),²³⁸ graphene oxides (sensitive to 4% RH under 11–95% RH range),²³⁹ organic small molecules (sensitivity of 2.5% in 0–95% RH range),⁵⁵ and conjugated polymers (sensitive to 1% RH in 33– 97% range).^{240–241} In the dark, gravimetric responses of ZnO/SU-8 nanocomposite films were completely reversible after 1 hour of gas/vapor desorption. Under UV irradiation, responses of ZnO/SU-8 films were over 80% reversible after 1 hour of water desorption, and $\sim 50\%$ reversible after 80 min of oxygen desorption (Figure 27(a) and (b)). The increased analyte adsorption under UV irradiation requires a longer desorption period, resulting in the lack of full reversibility between gas/vapor pulses under UV light. Improving the reversibility of ZnO-based gas sensors is generally achieved by thermally induced desorption, which may be investigated for the hybrid nanocomposite films in future studies. To examine the kinetics of gas/vapor adsorption, the frequency shift of ZnO-infiltrated SU-8 films during O₂/H₂O exposure was fit to an exponential model

$$\Delta f = \Delta f_0 + Ae^{-t/\tau} \quad (2)$$

where τ is the characteristic time constant for adsorption and A and Δf_0 are scaling and offset constants. The gravimetric response during gas/vapor adsorption is well explained by the exponential model ($r^2 > 0.985$) at each pressure under each environmental condition. The value of τ extracted during

adsorption in the dark and under UV irradiation is shown in Figure 30(b). Under UV irradiation, τ generally decreased with gas/vapor pressure, which suggests that the adsorption rate is diffusion-limited.²⁴² The average value of τ , after ~60 min under UV irradiation and ~20 min in the dark, is roughly an order of magnitude greater than the response times reported for other ZnO nanostructure-based sensors, including those for humidity and VOC, which typically exhibit response and recovery times on the order of 2 min^{208, 227} and the response time of capacitive SU-8 humidity sensors increasing with increasing level of cross-linking in the SU-8 matrix.²¹⁹ The large τ values measured here likely result from low analyte diffusion rates through the film due to a combination of the ZnO accumulation and the high level of polymerization in the SU-8 matrix. Under UV irradiation, τ generally decreased for higher numbers of ZnO-infiltration synthesis cycles likely due to more available infiltrated ZnO.

The clear separation between τ surfaces in Figure 30(b), which correspond to each of the four tested environmental conditions, suggests that τ can be used for distinguishing between different ambient environmental conditions based on the response of each film. Classification of the four environments was carried out using a support vector machine (SVM) algorithm with radial basis function kernel. The SVM was implemented using the Scikit-learn module in Python using 5-fold cross-validation to prevent overfitting.²⁴³ Using the number of ZnO-infiltration cycles, the gas/vapor pressure, and the value of τ as input variables, the SVM classified each of the four environments (O_2 in the dark, O_2 under UV irradiation, H_2O in the dark, and H_2O under UV irradiation) with over 96% accuracy. Considering the relatively small number of training points for the SVM (i.e., 5 gas/vapor pressures, 4 different infiltration cycles, 20 values of τ for each environment), it is expected that the environmental classification can reach 100% accuracy with a larger quantity of training data. The results demonstrate the possibility of using the ZnO-infiltrated hybrid SU-8 films with different levels of

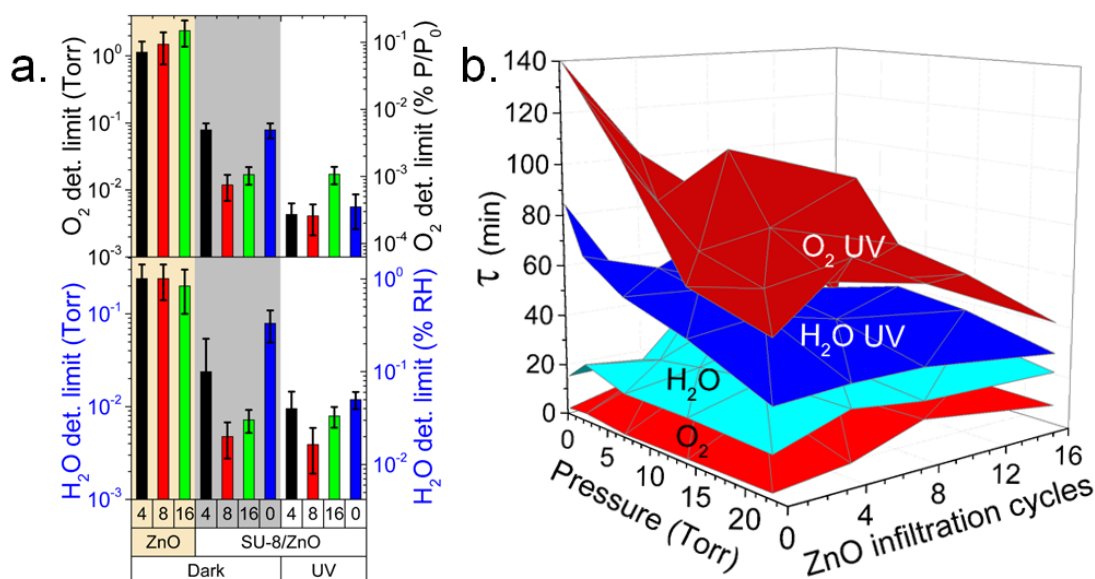


Figure 30. (a) Estimated detection limits for O_2 (top panel) and H_2O vapor (bottom panel) sensing using ZnO-infiltrated hybrid SU-8 films. The left vertical axes correspond to O_2/H_2O partial pressures, and the right vertical axes O_2 partial pressure in units of % P/P_0 (where P_0 is partial pressure of oxygen in atmosphere, ~ 160 Torr) (top) and % RH at 27°C (bottom). Note the use of log scales. The yellow shaded region corresponds to the control ALD ZnO films, the gray region to ZnO-infiltrated SU-8 films in the dark, and the white to ZnO-infiltrated SU-8 under UV irradiation. The numbers on horizontal axis correspond to the number of ZnO-infiltration synthesis cycles. Error bars correspond to amplitude of noise in frequency shift measurements. (b) Time constant (τ) measured from frequency shift during the adsorption of H_2O/O_2 in the dark and under UV irradiation. Figure reproduced with permission.²²⁶

infiltration as sensing arrays for accurate classification of ambient environmental conditions.

Optical and electrical properties

Finally, the effects of ZnO-infiltration synthesis on the optical and electrical properties of SU-8 films were investigated. Along with the demonstrated enhancement in gravimetric gas/vapor sensing performance, the information should guide the potential application of ZnO-infiltrated hybrid SU-8 films as multifunctional sensing media. The confocal Raman spectroscopy of ZnO-infiltrated SU-8 films (on SiO₂/Si substrates; 633 nm excitation wavelength) featured a broad photoluminescence band at 1690 and 2450 cm⁻¹ (~4.1–5.9 μm wavelength)²²⁶, which has been associated with defect states in bulk and epitaxial ZnO²⁴⁴ or quantum-confined ZnO nanoparticles.²⁴⁵ To further confirm the effect of ZnO-infiltration synthesis on the photoluminescence spectra of SU-8 films, the mean-centered principal component analysis (PCA) was performed on the spectra. A nonlinear iterative partial least squares algorithm with leverage correction validation was used for decomposition of eigenvectors during PCA. Two principal components (PC1 and PC2) explained 98% of the differences between experimental spectra²²⁶. Films without the low-frequency (1690–2450 cm⁻¹) feature in the Raman/photoluminescence spectra are clustered near the intercept corresponding to PC2 = 0 (red region), whereas the SU-8 films with ZnO infiltration contain the contributions from both components (blue region) in the spectral features. There is a clear distinction between ZnO-containing SU-8 films, pure ZnO, SU-8, and SiO₂, which suggests that photoluminescence from ZnO-infiltrated SU-8 is influenced by morphological or optoelectronic interaction between ZnO and SU-8. The higher PC2 contribution to spectral features of 8 cycle ZnO-infiltrated SU-8 compared to that of 16 cycle-infiltrated SU-8 suggests that interaction between infiltrated ZnO and the SU-8 matrix is not strongly

correlated with the number of ZnO-infiltration synthesis cycles. Multivariate curve resolution (MCR) performed without an initial guess on photoluminescence spectra revealed two optimal spectral components²²⁶, in agreement with results of PCA. The MCR enabled separation of two spectral features in the photoluminescence spectra, which are likely associated with ZnO species (low-frequency feature with a peak around 1450 cm⁻¹).

We investigated the electrical properties of ZnO-infiltrated hybrid SU-8 films by measuring the DC electrical resistance in ambient air in the dark and under UV irradiation. In the dark, the DC resistance of SU-8 film is ~108 Ω (Figure 31(a)). After four ZnO-infiltration synthesis cycles, the resistance decreased by ~5 orders of magnitude to ~103 Ω . Subsequent infiltration cycles did not significantly alter the resistance, which suggests that four cycles of infiltration resulted in the formation of conductive ZnO pathways, allowing electrical conduction. After 8 and 16 infiltration cycles, the resistance of ZnO-infiltrated film was roughly equal to that of the control ALD-prepared ZnO films, likely because of the highly ZnO-concentrated top dense layer formed at the hybrid film surface. Interestingly, there was a UV-induced increase in the resistance of ZnO-infiltrated SU-8 film, whose extent was diminishing for the larger number of infiltration synthesis cycles (Figure 31(b)). The un-infiltrated SU-8 film exhibited a large (~34%) increase in resistance during UV exposure, which we expect was caused by the UV-induced decomposition of the charged (Ar)₃S⁺SbF₆⁻ PAG. The degree of UV-induced resistance increase was reduced with more ZnO-infiltration synthesis cycles, which is in line with the notion that ZnO accumulation near the film surface acted as a UV-blocking layer, passivating the underlying SU-8. From 0 to 4 ZnO-infiltration cycles, the percent change in resistance decreased by a factor of ~100,²²⁶ which show that four cycles provided enough ZnO for the creation of conductive pathways near the film surface. Meanwhile, the control ALD ZnO films displayed negligible change in resistance upon UV exposure (Figure 31b), most

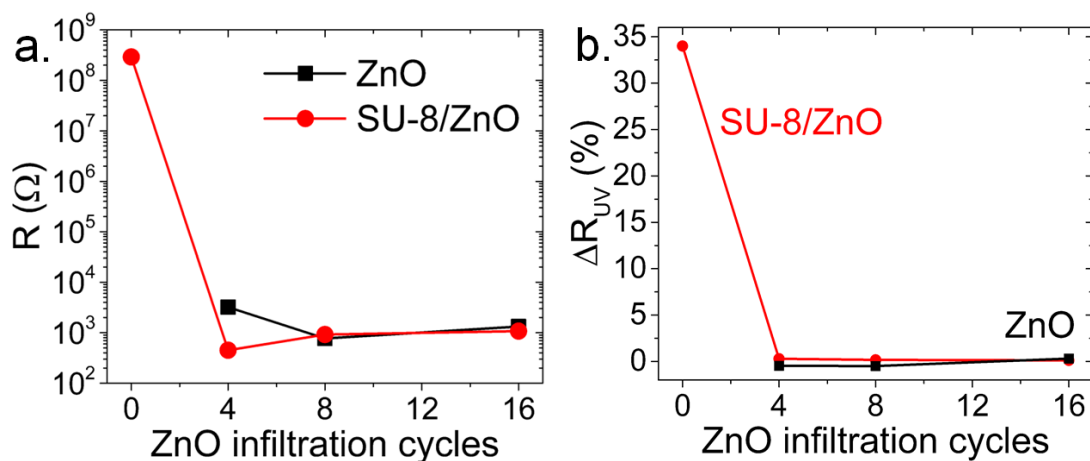


Figure 31. (a) DC electrical resistance of control ALD-mode-prepared ZnO films and ZnO-infiltrated hybrid SU-8 films measured in the air in the dark as a function of the number of infiltration synthesis cycles. The ZnO-infiltrated SU-8 film with 0 infiltration cycle corresponds to the un-infiltrated SU-8 film. (b) DC electrical resistance change (ΔR_{UV}) after 10 min of UV irradiation for control ZnO films and ZnO-infiltrated hybrid SU-8 films. Figure reproduced with permission.²²⁶

likely due to nominal small thickness (i.e., < 1.6 nm assuming $1 \text{ \AA/cycle}$ deposition rate for normal ALD), which limited UV adsorption.

Conclusions

Infiltration synthesis of ZnO in SU-8 thin films generated organic–inorganic hybrid nanocomposites displaying UV-enhanced gravimetric sensing behavior. UV irradiation leads to reversible photowetting and improved sensing properties of SU-8 polymer alone. The gravimetric response of ZnO-infiltrated hybrid SU-8 films was ~ 20 times higher than that of the un-infiltrated control SU-8 film during exposure to water vapor and oxygen. The response was enhanced by an additional 50–500% under UV irradiation. We proposed that in case of composite film, the increased adsorption sites were provided by the infiltrated ZnO nanoparticles in SU-8 matrix, in conjunction with the reversible UV-induced decomposition of the PAG in SU-8 into hydrophilic fluoroantimonic acid leading to increase in the adsorption affinity toward oxygen and water (corroborated with DFT calculations), as the primary mechanisms that enabled high gravimetric vapor/gas sensing performance of ZnO-infiltrated SU-8 film. We further demonstrated that under illumination SU-8–ZnO composites can (without additional modifications) differentiate between water vapor and oxygen gas with over 96% accuracy. The results also not only represent a new application of the inorganic–organic hybrid nanocomposite generated by infiltration synthesis as a highly sensitive gravimetric vapor/gas sensing medium, but also shed light on the possibility of using reversible UV-induced chemical changes to tune hydrophilicity for modifying selectivity and sensitivity of thin films for sensing applications.

Chapter 8: Humidity response of H-intercalated MXene

A version of this chapter was originally published by Eric Muckley, Michael Naguib, and Ilia Ivanov:

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Michael Naguib synthesized the Ti_3C_2 MXene. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Materials synthesis was supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

Abstract

Gravimetric, direct-current electrical, and electrical impedance sensing modes were used to measure response of high surface area 2D Ti_3C_2 MXene film to water vapor pressures spanning 3 orders of magnitude (20 mTorr - 20 Torr). The Ti_3C_2 film exhibited reproducible reversible response in 0.1%-95% relative humidity (RH) range with a detection limit of < 20 mTorr H_2O partial pressure (< 0.1% RH). DC electrical current-based sensing with 3 mV operating voltage and 0.8 pW power consumption was demonstrated. The highest normalized sensitivity was shown for gravimetric sensing modalities which scale with the overtone number, reaching highest sensitivity of about 12 Hz / % RH at the 9th crystal overtone (45 MHz oscillation).

Introduction

A new class of two-dimensional (2D) transition metal carbides and carbonitrides termed MXenes is being explored for use in a wide range of electrochemical applications²⁴⁶. Because of high surface area and tunable terminations/ion intercalants, MXenes have been investigated for chemical sensing of sodium nitrite²⁴⁷, ammonia²⁴⁸, glucose²⁴⁹, and hydrogen peroxide²⁵⁰. The most widely-studied MXene to date, Ti_3C_2 , exhibits strong hydrophilicity and high electrical conductivity²⁵¹. Experimental and computational studies have confirmed the presence of mixed -OH, -O, and -F terminations in Ti_3C_2 films which provide hydrophilic sites for water adsorption^{246, 252-257}. Although these properties make Ti_3C_2 MXene well-suited for relative humidity (RH) sensing, much research on the H_2O response of Ti_3C_2 has been limited to studies of ion-intercalated Ti_3C_2 ^{38, 251}. Ghidui et al. reported on effect of water on Ti_3C_2 structure but did not correlate mechano-structural response to electrical or functional response²⁵⁸. Come et al. showed that adsorption of water can lead to stiffening of Ti_3C_2 film due to formation of highly ordered water layers between Ti_3C_2 sheets²⁵⁹ but did not relate this effect to sensing performance. Römer et al. reported a linear increase in Ti_3C_2 resistivity as RH increased from 15-80%²⁶⁰.

Ghidui et al. showed that K^+ , Na^+ , Li^+ , Ca^{2+} -intercalated Ti_3C_2 undergoes an increase in basal spacing during water intercalation between 2D Ti_3C_2 sheets, and the amount of adsorbed water, referenced to the molecular weight of ion-intercalated $\text{Ti}_3\text{C}_2\text{T}_x$, does not depend on the nature of intercalated ion²⁵¹. Shpigel et al. reported negligible viscoelastic changes of Ti_3C_2 film in air under low humidity conditions²⁶¹. However, it remains unclear how adsorbed water influences viscoelastic behavior of Ti_3C_2 films, and dynamic range and detection limits for Ti_3C_2 -based humidity sensors have not been thoroughly investigated. We showed previously that K^+ and Mg^{2+} ion intercalated Ti_3C_2 film exhibited

electrical and gravimetric response to water vapor between 20% and 80% RH³⁸. However, dynamic range, detection limits, reversibility, and long-term stability and repeatability of non-intercalated Ti₃C₂- humidity sensors were not investigated in detail. Here we present the results on correlation between gravimetric and electrical response of Ti₃C₂ films to humidity, addressing important question of detection limits, operable range, reversibility, and long-term stability/repeatability of Ti₃C₂-based gravimetric and electrical RH sensors. As evidenced by modeling of multi-frequency gravimetric response, Ti₃C₂ film exhibits a gradual transition from rigid to viscoelastic behavior as humidity increases.”

Other 2D materials including VS₂²⁶², MoS₂²⁶³, and black phosphorus nanosheets²⁶⁴ exhibit strong response to water vapor but their operable range as RH sensors is tested only for RH > 10% (corresponding to ~3000 ppm H₂O partial pressure). Response to 1% RH has been observed in graphene²⁶⁵, but sub-1% RH detection limits are seldom reported. In this study, we demonstrate gravimetric response of Ti₃C₂ to 0.1% RH, corresponding to ~30 ppm H₂O partial pressure. We investigated the humidity range under which Ti₃C₂ film may be used for reversible RH sensing and probed detection limits for both gravimetric and electrical sensing modes. We used multi-harmonic quartz crystal microbalance with dissipation monitoring (QCM-D) to correlate Ti₃C₂ sensor response with viscoelastic behavior in the Ti₃C₂ film.

Experiment

Details of Ti₃AlC₂ synthesis were described elsewhere by Naguib et al.²⁶⁶. For synthesis of Ti₃C₂ used in this study, Ti₃AlC₂ was etched using a solution of LiCl dissolved in 10 wt% HF (1 g Ti₃AlC₂/10 mL of etching solution and Ti₃AlC₂/LiCl ~ 1:5 molar ratio) at room temperature for 24 hours. After etching, the mixture was

centrifuged, the top liquids were decanted, fresh deionized water was added to the settled powder, then centrifuged, and the top liquids were decanted. The washing steps were repeated until the pH of the top liquids reached values > 5 . Settled powder was then rinsed with 37% HCl (30 mL of 37% HCl: 1 g of powder) then centrifuged. Liquids were decanted and the rinsing process using HCl was repeated four times to remove extra salts from the etching process and to remove any intercalated Li ions and replace them with protons. This was followed by rinsing with deionized water. The wet powder was vacuum filtered to dry. Dry Ti_3C_2 was mixed with deionized water to produce 34% Ti_3C_2 by weight solution. For gravimetric and viscoelastic measurements, 1 μL of solution was drop-cast on pre-cleaned 5 MHz-resonant frequency AT-cut gold-coated quartz crystal microbalance (QCM) crystals. For electrical measurements, 1 μL of solution was drop-cast on undoped SiO_2 substrates with pre-patterned 2 μm -spaced gold interdigitated electrodes (for resistivity and passive sensing experiments) and pre-patterned 1 cm-spaced gold electrodes for impedance spectroscopy measurements. Deposition of Ti_3C_2 film resulted in a porous network of conductive pathways with up to ~ 5 μm thick. All synthesis, preparation and experiments were conducted at room temperature.

For testing, Ti_3C_2 -coated QCM and pre-patterned electrodes were placed under 10^{-4} Torr (1.33×10^{-7} bar) vacuum for 12 hours before exposure to water vapor. Fundamental QCM frequency shift was recorded using an openQCM Pierce oscillator circuit³⁷. DC resistivity and passive current measurements were performed using a Keithley 2420 source-meter with 20 mV and 3 mV bias respectively. Electrochemical impedance spectroscopy (EIS) was performed using a Zahner IM6 electrochemical workstation. Humidity was controlled by injecting water vapor into the vacuum chamber at 20 cm^3/min flow rate using a mass flow controller. A LabVIEW program was used to control the H_2O flow and record resistivity of the film and frequency shift of the QCM during the experiment. For viscoelasticity measurements, frequency and dissipation were

recorded at 1st, 3rd, 5th, 7th, and 9th crystal harmonics for a Ti₃C₂-coated 5 MHz QCM crystal inside a KSV QCMZ-500 liquid flow cell while humidity was varied using an L&C RH-200 humidity generator with dry N₂ as a carrier gas.

Results and discussion

DC resistive and gravimetric sensing

Electrical resistance of Ti₃C₂ film (ΔR) and fundamental frequency shift (Δf) of Ti₃C₂-coated QCM were measured under changing RH conditions. When RH was increased from ~0% to 95%, frequency shift of the Ti₃C₂-coated QCM was ~50 times higher than that of the bare Au reference QCM (Figure 32(a)), indicating selective adsorption of H₂O on Ti₃C₂ likely due to its relatively high surface area (10-20 m²/g) and hydrophilic surface-terminating functional groups (OH, O, and H)²⁴⁶. Values of Δf and ΔR were observed under H₂O partial pressures spanning a range of 3 orders of magnitude (20 mTorr – 20 Torr) (Figure 32(a)) bottom panel). Gravimetric (Δf) and resistive (ΔR) responses decreased exponentially with RH (Figure 32(b)), indicating that the strongest RH response of Ti₃C₂ occurred under dry (< 20% RH) conditions. Previous experimental and theoretical results showed that adsorption of ~2 H₂O molecules per unit cell in ion-intercalated Ti₃C₂ resulted in significant structural and electrical changes³⁸. The small electrical resistance change (~1.75 Ω) from 0-95% RH was ~0.8% of the total resistance of the film (~200 Ω), indicating that conductive Ti₃C₂ with small electrical response can still be effective as a wide-range RH sensing material.

To estimate detection limits of gravimetric- and resistive- Ti₃C₂ sensors, 30 second integration time was used to decrease signal to noise ratio (SNR).

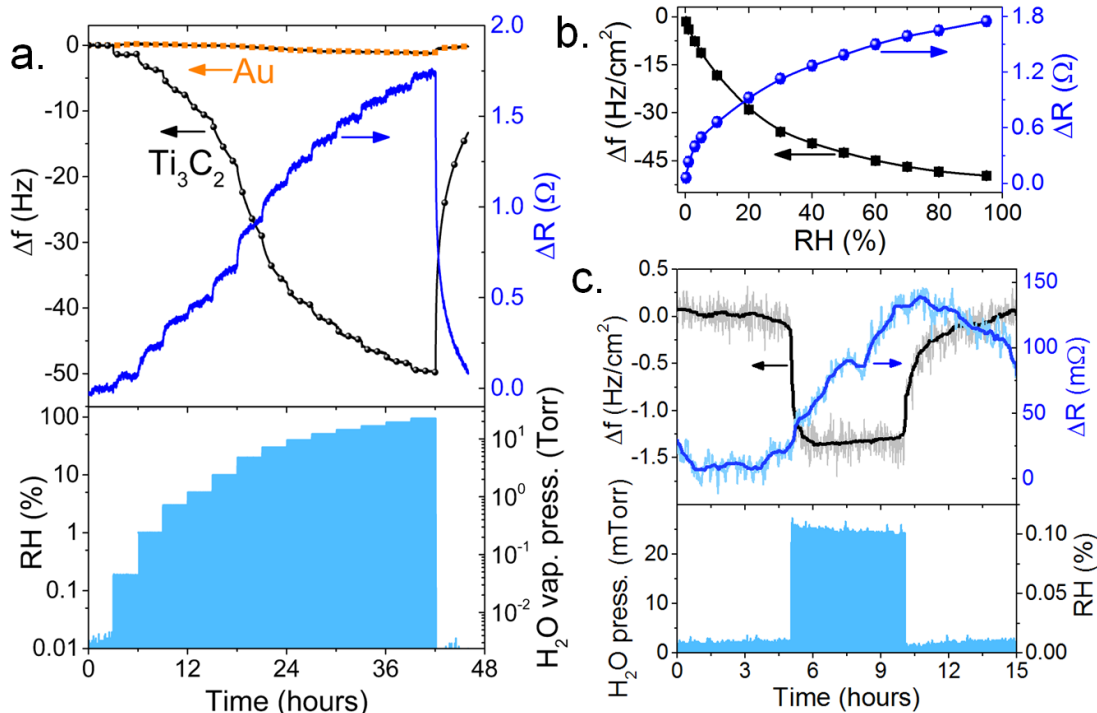


Figure 32. (a) Top panel: Fundamental frequency shift (Δf , left axis) of Ti_3C_2 -coated QCM and bare Au-coated QCM during exposure to water vapor partial pressures spanning over 3 orders of magnitude (bottom panel). Right axis of top panel shows DC electrical resistance change (ΔR) of Ti_3C_2 film. Water concentration in bottom panel is shown in terms of relative humidity (RH) and H₂O vapor pressure. (b) Fundamental frequency shift (black, left axis) and electrical resistance change (blue, right axis) measured from 0-95% RH after 3 hours of exposure to each RH level. (c) Frequency shift and resistance change during exposure to single H₂O vapor pulse (bottom panel) corresponding to ~25 mTorr H₂O vapor pressure (0.1% RH). Solid dark lines show response after 50-point adjacent averaging. Figure reproduced with permission.²⁶⁷

Increasing the integration time without loss of important temporal information was possible due to the slow H₂O response kinetics shown in Figure 32(c). Upon exposure to a ~25 mTorr H₂O vapor pulse (corresponding to ~0.1% RH) (Figure 32(c) bottom panel), Ti₃C₂-coated QCM exhibited fundamental frequency shift of ~1.3 Hz/cm² corresponding to mass change of ~23 ng/cm² under Sauerbrey conditions³⁶, and electrical resistance of the Ti₃C₂ film increased by ~140 mΩ. Although the frequency shift and resistance change are small compared to those reported for typical thin film resistive and QCM-based RH sensors^{40, 55-56, 58}, Δf and ΔR exhibited signal-to-noise ratios SNRs of ~5 in response to the 0.1% RH pulse which demonstrates that Ti₃C₂ may be used as a RH sensing material under an extremely broad range of humidity levels (0.1%-95% RH). While Δf and ΔR kinetics occurred over the scale of ~1 hour at RH > 20% (Figure 32(a)), change in Δf occurred over 1-2 hours and change in ΔR occurred over a period of over 5 hours when RH was increased from 0.01% to 0.1%. This suggests that at low water vapor partial pressure, capillary action which drives H₂O diffusion between individual 2D Ti₃C₂ layers is severely limited³⁸.

To probe long-term sensor stability and reproducibility, gravimetric response of the Ti₃C₂ film was recorded during repeated cycling from 20% to 80% RH. After 20 cycles over a duration of 18 hours, the film showed repeatable response within 6%²⁶⁸. Long-term stability of the film was probed by exposing sensor to constant RH level for 12 hours steps and recording resonant frequency of the Ti₃C₂-coated QCM. Gravimetric response of the film was stable to within 6% over a period of 12 hours²⁶⁸.

Frequency-dependent electrical sensing

To investigate the mechanism of electrical response of Ti₃C₂ to water, electrical impedance spectroscopy (Z) was measured from 100 Hz – 4 MHz using

20 mVAC excitation with 0 VDC bias at 0, 5, 20, 40, 60, 80, and 95% RH. The effect of RH on impedance was most pronounced at low frequency (100 Hz), followed a roughly exponential increase with RH, and showed ~100% reversibility after water vapor was removed (Figure 33(a)) from the measurement chamber, in agreement with RH-dependent DC resistivity measurements. The semi-circle in the Nyquist plot (Figure 33(b)) is a signature of combined effects of resistive (R) and capacitive (C) elements, which may be modeled by an equivalent double RC circuit (shown in inset of Figure 33(b)) composed of contact resistance (R_C), resistance and capacitance associated with conduction through Ti_3C_2 grains (R_G and C_G respectively), and resistance and capacitance associated with conduction across grain boundaries (R_{GB} and C_{GB} respectively)⁶³. The dominance of a single semi-circle in the Nyquist plot, along with the high conductivity of Ti_3C_2 ²⁶⁹, suggests that the majority of resistance and capacitance is associated with conduction across grain boundaries while bulk Ti_3C_2 grains contribute insignificantly to the film impedance. The resistive (Figure 33(c)) and capacitive (Figure 33(d)) values of equivalent circuit parameters demonstrate that while impedance of the conductive bulk grains changed insignificantly during RH exposure, both R_{GB} and C_{GB} increased with RH. RH-dependence of R_{GB} and C_{GB} closely resembled that of Z and DC electrical resistance which suggests that water accumulation near gain boundaries is the primary mechanism underlying Ti_3C_2 electrical response to water. The value of R_C which is generally associated with conduction at film domain-electrode junctions²⁷⁰ showed a slight increase with RH,²⁶⁸ indicating a voltage drop due to accumulation of adsorbed water at gold- Ti_3C_2 junctions. X-ray diffraction patterns (not shown) revealed no significant difference between dry Ti_3C_2 and Ti_3C_2 exposed to water, suggesting that that H_2O molecules did not intercalate between individual 2D Ti_3C_2 sheets, as expected.

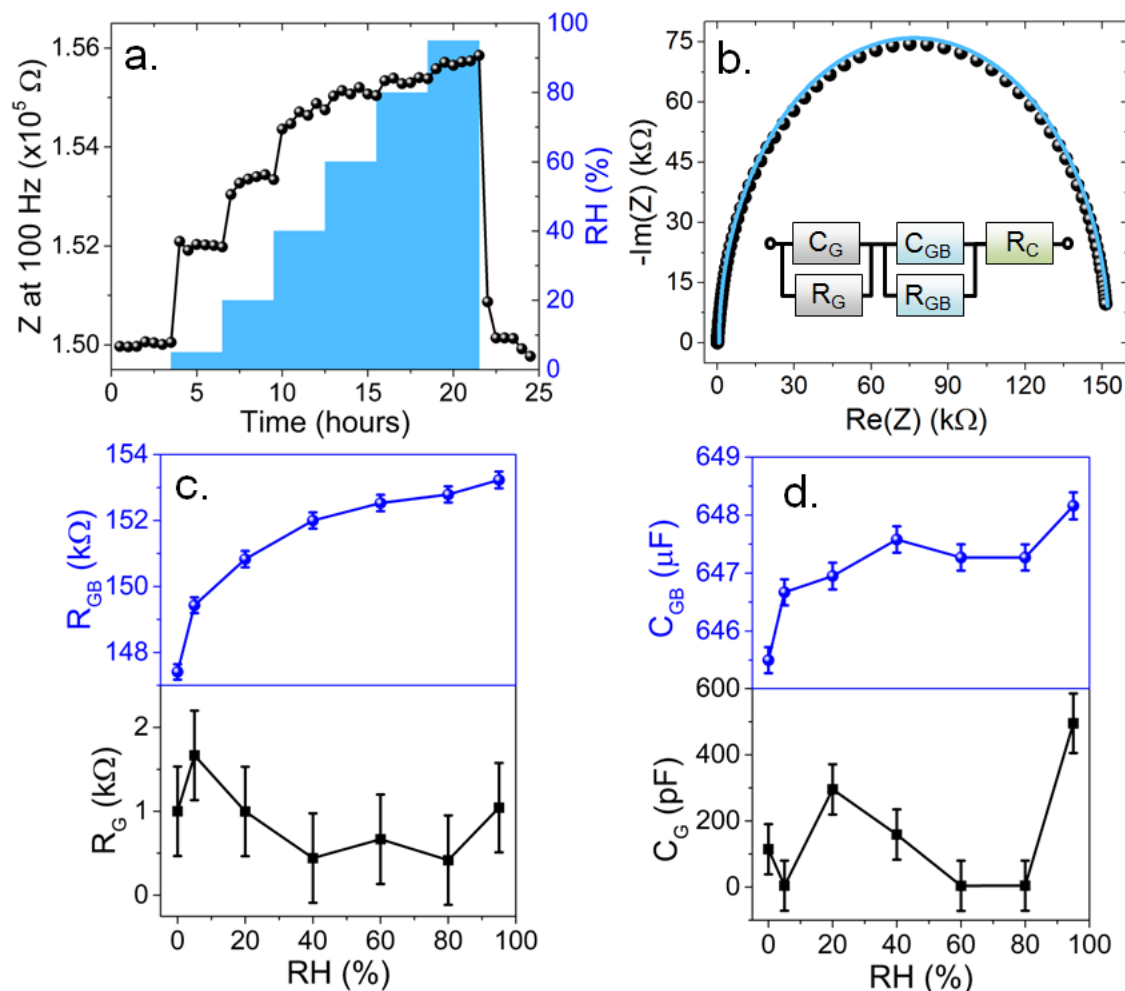


Figure 33. (a) Impedance (Z) of Ti_3C_2 film measured at 100 Hz during exposure to 0, 5, 20, 40, 60, 80, 95% RH (blue, right axis). (b) Nyquist representation of impedance of Ti_3C_2 film (black points) fitted to double RC equivalent circuit (blue line). Inset shows equivalent circuit model composed resistance and capacitance in bulk grains (R_G , C_G), resistance and capacitance at grain boundaries (R_{GB} , C_{GB}), and resistance at contacts (R_c). (c) Values of R_{GB} and R_G extracted from equivalent circuit fits. (d). Values of C_{GB} and C_G extracted from equivalent circuit fits. Error bars correspond to uncertainty introduced during fitting of equivalent circuit model. Figure reproduced with permission.²⁶⁷

Low-power current sensing

Low electrical resistivity ($\sim 20 \Omega \cdot \text{cm}$) and strong response to water vapor enabled passive Ti_3C_2 -based RH sensing with negligible power consumption. We applied constant 3 mV DC bias across Ti_3C_2 film and monitored picoamp-scale changes in electrical current (ΔI) under changing RH conditions (Figure 34(a)). Current decreased by ~ 260 pA when RH increased from 0-95% and showed reversible, reproducible response to changing RH conditions as RH was cycled from 0, 40, 95% and back to 0%. SNR in electrical current response is ~ 5 during response to 40% RH and ~ 7 during response to 95% RH, which enable $\sim 10\%$ RH resolution by passive (~ 3 mV) sensors in the 0-95% RH range. The value of ΔI followed a roughly double exponential trend with RH (Figure 34(b)), in agreement with low-frequency impedance and DC electrical resistance measurements. The 3 mV operational voltage is small enough to be supplied by entirely passive energy-harvesting devices including radio-frequency identification (RFID) antennas²⁷¹, vibrational micro-generators²⁷², and piezoelectric fabrics and textiles²⁷³. Total power consumption of the $3 \text{ mV} \times 260 \text{ pA}$ sensor is $\sim 0.8 \text{ pW}$ which is roughly the average power consumption of a human cell. The inset of Figure 34(b) shows that current-voltage characteristics of the Ti_3C_2 film from -1 to 1 V DC bias are linear, which suggests that passive RH sensors which rely on ambient energy harvesting devices may maintain linear current response even under variable power conditions.

Mechanism of gravimetric response to water vapor

We used quartz crystal microbalance with dissipation monitoring (QCM-D) for probing frequency shift (Δf) and dissipation change (ΔD) of Ti_3C_2 -coated QCM at 1st, 3rd, 5th, 7th and 9th crystal harmonics to investigate whether exposure to high humidity conditions caused any observable viscoelastic changes in the sensing

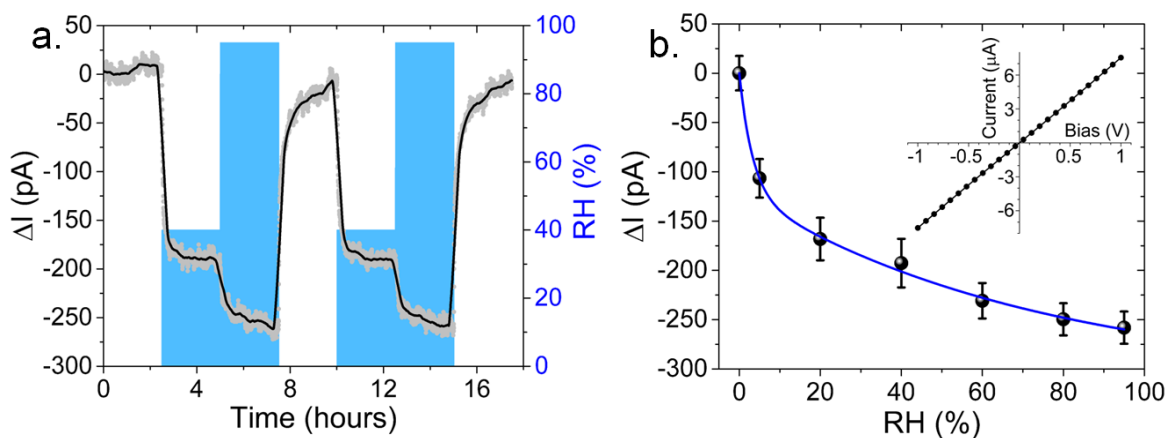


Figure 34. (a) Change in current (ΔI) measured across Ti_3C_2 film under 3 mV DC bias. Gray points show measured current, black line shows current after smoothing by 50-point adjacent averaging. Blue pulses (right axis) correspond to 0, 40, and 95% RH. (b) Current change showed roughly double exponential trend with RH (blue line). Error bars represent amplitude of noise in current signal. Inset: Ti_3C_2 film showed linear current-voltage characteristics from -1 to 1 VDC bias. Figure reproduced with permission.²⁶⁷

film. A thin homogenous film rigidly-bound to the QCM surface undergoes frequency shift which is proportional to mass change in accordance with the Sauerbrey equation³⁶. Under Sauerbrey conditions, Δf and ΔD are harmonic-independent and thus show negligible variation between harmonics after normalization to harmonic number²⁷⁴. This was observed in QCM-D measurements performed on a bare Au-coated QCM from 5%-90% RH,²⁶⁸ which indicated that changes in resonant frequency of the bare Au crystal were strictly a result of mass loading of the resonator.

The QCM coated with Ti_3C_2 film exhibited significant harmonic-dependent frequency shift and dissipation change in response to changing RH,²⁶⁸ indicating viscoelastic change in the Ti_3C_2 film²⁷⁴. The frequency shift and dissipation change during H_2O adsorption on bare Au were subtracted from Δf and ΔD values measured on the Ti_3C_2 -coated crystal to remove the effects of changing density and viscosity of humid air and to isolate the effect of water on viscoelastic response of Ti_3C_2 . Normalized $\Delta f/n$ and $\Delta D/n$ (where n is harmonic number) shown in Figure 35(a) exhibited harmonic-dependence which increased with increasing RH. The slope $\Delta D/\Delta f$ was used to estimate energy dissipation per unit mass of the Ti_3C_2 film²⁷⁵. Significant deviations from the linear relationship between ΔD and Δf generally occurred near 50% RH,²⁶⁸ which suggests the onset of structural/conformational changes, viscoelastic changes, or interface slip between Ti_3C_2 film and the gold electrode.^{38, 258, 269-270}

The simplest way to account for nonlinear mass loading of the resonator is to treat the film/water adlayer as a viscous liquid using the Kanazawa-Gordon equation³⁹: $\Delta f = f_0^{3/2}(\rho\eta/\pi\mu_q\rho_q)^{1/2}$, where ρ and η are density and absolute viscosity of the effective liquid and μ_q and ρ_q are shear modulus and density of the quartz resonator. We used frequency shift of the fundamental resonant frequency (Δf_1) to estimate the corresponding Sauerbrey frequency shifts at higher harmonics by scaling Δf_1 linearly with harmonic number²⁷⁴. The deviation

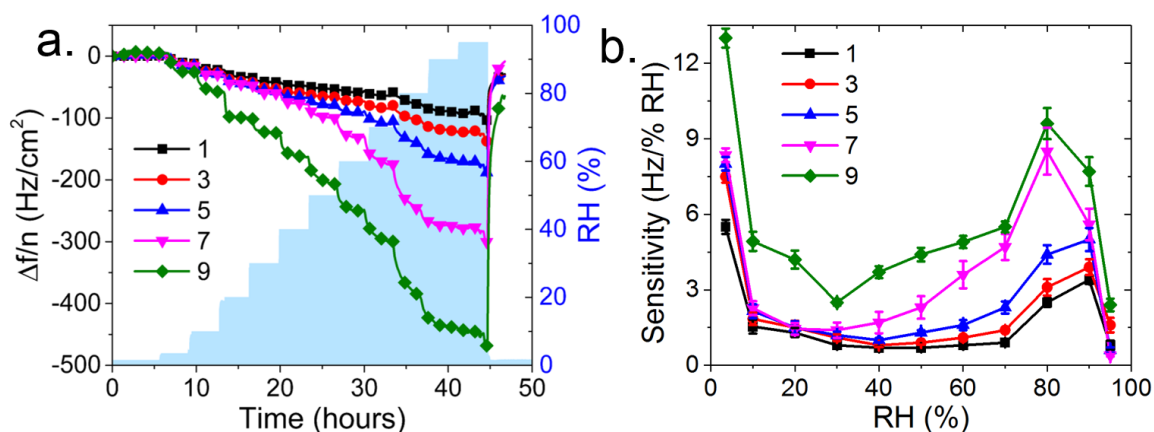


Figure 35. (a) Frequency shift normalized to harmonic number ($\Delta f/n$) of Ti_3C_2 -coated QCM during exposure to increasing RH levels (blue, right axes). Values of $\Delta f/n$ for bare Au QCM were subtracted to remove effects of water adsorption on Au and drag forces arising from changing density and viscosity of humid air. Legend shows crystal harmonic number. (b) Gravimetric sensitivity of Ti_3C_2 film to humidity estimated as a ratio of normalized frequency shift of 1st, 3rd, 5th, 7th and 9th harmonics over change in RH%. Figure reproduced with permission.²⁶⁷

between Sauerbrey frequency shift (Δf_s) and experimentally-measured frequency shift (Δf_{exp}) was used to estimate the frequency shift resulting from viscoelastic changes in the adlayer film as described by Kanazawa (Δf_k), so that $\Delta f_{\text{exp}} = \Delta f_s + \Delta f_k$.²⁶⁸ Using Δf_k and the Kanazawa-Gordon equation, we obtained estimates for $\Delta \eta\rho$, the change in product of effective viscosity and density of the Ti_3C_2 adlayer film under changing RH conditions (Figure 35(b)). The value of $\Delta \eta\rho$ increased with RH as water filled in pores in the Ti_3C_2 film and increased the average density. It is expected that the effective viscosity of the Ti_3C_2 adlayer increased with RH due to softening of the film by water. Water accumulation near Ti_3C_2 surfaces may disrupt van der Waals interactions between adjacent Ti_3C_2 domains, decreasing rigidity of the film and contributing to energy damping observed in measurements of ΔD . The ratio $\Delta f_k/\Delta f_s$ which compares the importance of viscoelastic effects to mass loading effects generally increases with RH.²⁶⁸ Higher order harmonics typically probe regions of the adlayer film which are closer to the crystal surface, since penetration depth of the acoustic wave into the adlayer film scales as $\sqrt{1/f}$.⁴⁴

We performed additional viscoelastic modelling of the Ti_3C_2 film using the approach of Voinova et al.³⁵ as described in the supporting information. The results suggest that viscoelastic effects are most pronounced close to the Ti_3C_2 /crystal interface. This is consistent with results from electrical impedance modelling which suggest that water accumulation at Ti_3C_2 /crystal interface led to changes in charge transfer resistance. Notably, observed viscoelastic change in the Ti_3C_2 film did not result in unpredictable behavior in gravimetric or electrical response of Ti_3C_2 to water, which suggests that Ti_3C_2 film may be used for wide-range RH sensing even under extreme RH conditions which induce viscoelastic changes in the film.

We compared sensitivity of all modalities using normalized sensitivity approach (Figure 36). Sensitivity of each sensing modality was first estimated as a slope of

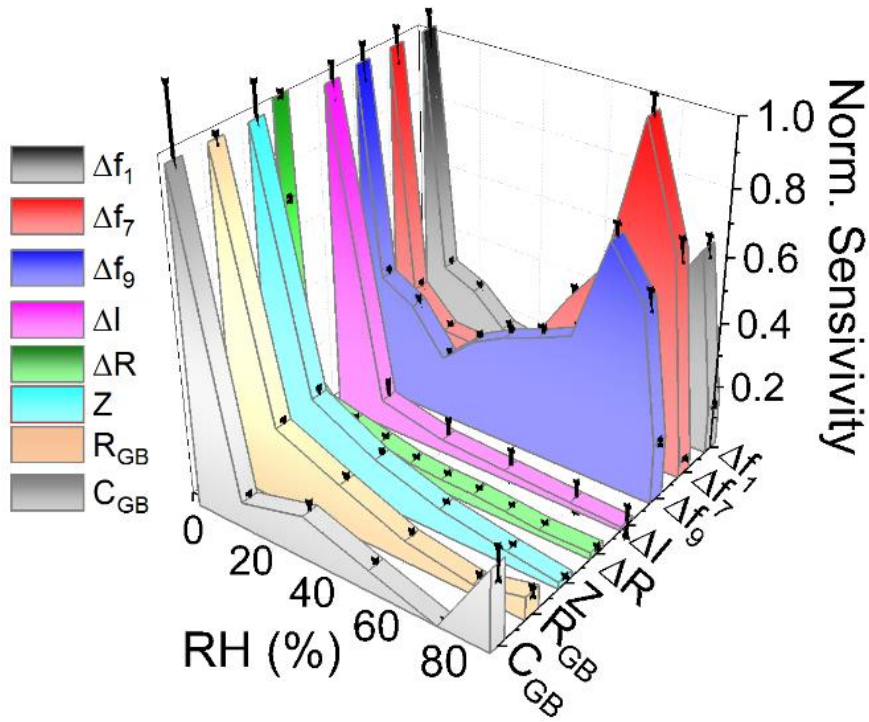


Figure 36. Sensitivity of Ti_3C_2 humidity sensing modalities. Normalized sensitivity = S/S_{max} , where S is sensitivity and S_{max} is maximum sensitivity achieved for a given sensing mode. Figure reproduced with permission.²⁶⁷

response over a given RH change and plotted against relative humidity²⁶⁸. Then, the sensitivity was normalized to maximum of sensitivity for each modality.

Majority of sensing modalities have similar normalized sensitivity for low range of humidities and smaller for mid and high humidity. The advantage of gravimetric over other sensing modalities is apparent and the 7th harmonic showing the best sensitivity over full humidity range.

Conclusions

We tested several reversible water sensing modes using Ti_3C_2 thin film. These modalities include multi-frequency gravimetric, DC-resistive, and frequency-dependent electrical response to adsorption of water from 20 mTorr H_2O partial pressure (0.1% RH) to 95% RH. Modelling of electrical impedance revealed that the primary mechanism behind electrical response of Ti_3C_2 was related to charge transfer resistance of the film due to adsorbed water at Ti_3C_2 -electrode interfaces. Low power DC resistance sensing modality was demonstrated at 3 mV operating voltage that could potentially be supplied by a passive energy-harvesting device. Using multi-harmonic QCM-D and modelling of Ti_3C_2 viscoelastic RH response, we showed that density and/or viscosity of the film increased during adsorption of water. Changes in viscoelastic properties of the film did not prevent reversible RH sensing behavior under the wide range of H_2O partial pressures which were probed. Among all tested modalities, the highest normalized sensitivity was shown for gravimetric sensing modalities.

Chapter 9: Humidity response of ion-intercalated MXenes

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All data shown in this chapter was acquired, analyzed and plotted by Eric Muckley. Michael Naguib synthesized the ion-intercalated Ti_3C_2 MXene. Results from imaging, neutron measurements, computer simulations, and liquid-based QCM measurements are available in the full publication³⁸. Materials synthesis, characterization, and calculations were as supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Electrical, gravimetric and thermogravimetric responses of MXene films were measured at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Research at the NOMAD beamline at ORNL's Spallation Neutron Source (SNS) was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Experiments on HFBS at NIST Center for Neutron Research (NCNR) were supported in part by the National Science Foundation under Agreement No. DMR-1508249. Certain commercial material suppliers are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the

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Abstract

Understanding of structural, electrical and gravimetric peculiarities of water vapor interaction with ion-intercalated MXenes led to design of a multimodal humidity sensor. Neutron scattering coupled to molecular dynamics and *ab initio* calculations showed that a small amount of hydration results in a significant increase in the spacing between MXene layers in the presence of K and Mg intercalants between the layers. Films of K and Mg-intercalated MXenes exhibited relative humidity detection thresholds of $\sim 0.8\%$ (RH) and showed monotonic RH response in the 0-85% RH range. We found that MXene gravimetric response to water is 10 times faster than their electrical response, suggesting that H₂O-induced swelling/contraction of channels between MXene sheets results in trapping of H₂O molecules that act as charge-depleting dopants. The results demonstrate the first use of MXenes as humidity sensors and infer potential impact of water on structural and electrical performance of MXene-based devices.

Introduction

MXenes are large family of 2-dimensional (2D) materials of transition metal carbides and carbonitrides.^{246, 266, 276} MXenes are produced by etching A layers from MAX ($M_{n+1}AX_n$) phases,^{266, 276} where *M* is an early transition metal, A is a group IIIA or IVA element, and X is carbon or nitrogen with *n* = 1, 2, or 3.²⁷⁷ Of over a dozen different MXenes synthesized to date, the most widely-investigated

MXene is Ti_3C_2 ,²⁶⁶ which has garnered attention for its exceptional performance in supercapacitors, batteries, water purification, composites for flexible electronics, and sensors.^{246, 251, 278-282}

MXenes are electrically conductive and capable of hosting a wide variety of ionic^{246, 251} and molecular species in their galleries.²⁸³ MXenes surfaces are terminated by O, OH, and F making them hydrophilic.^{252, 284} Of particular interest is H_2O sorption/intercalation, which could lead to significant structural and electrochemical changes in properties of MXene films.^{251, 285} Understanding the H_2O -MXene interaction is complicated by saturation of MXene flakes by hydrophilic surface groups²⁸⁶ and coordination of H_2O to intercalated cations.²⁵¹ The presence of cations intercalated between individual MXene sheets influences H_2O diffusion during hydration/dehydration processes²⁸⁵ and affects H_2O -induced swelling in multi-layered MXene sheets.²⁵¹ However, it is still unclear if interaction with H_2O affects the chemical composition of MXenes. In TiC , even the least reactive crystal face reacts with adsorbed H_2O leading to formation of TiO_2 , CO , CO_2 , and H_2 .²⁸⁷⁻²⁸⁸

While effects of H_2O sorption on the *c*-lattice parameters of MXenes have been studied,^{251, 285} the electronic effects originating from H_2O exposure are less understood, especially in the presence of intercalated ions. Adsorption of oxygen on titanium carbide surfaces can lead to O_2 dissociation due to charge transfer between O and Ti,^{284, 286} so one would expect that dissociative interaction of MXene surfaces with H_2O may also lead to complex charge transfer effects.

Despite their hydrophilic nature and tunable electrical properties, MXenes have not been explored for gas or humidity sensing applications. This could be due to their high conductivity,²⁴⁶ which may limit electrical response to gas/vapor adsorption. The ability of ion-intercalated MXenes to take up H_2O between stacks of multi-layers and individual exfoliated layers²⁸⁵ makes MXenes attractive

candidates for relative humidity (RH) sensing. Understanding the hydration/dehydration and corresponding electrical response of MXenes is crucial for the design of MXene-based electronics and environmental sensors. Here we report resistive H₂O response of Ti₃C₂ MXenes intercalated with K and Mg cations. We correlate the resistive response to gravimetric-based relative humidity (RH) sensing using a quartz crystal microbalance (QCM) with sub-0.1 Hz resolution.

Experiment

Intercalated MXenes used in this study were synthesized similar to those reported by Ghidui et al.²⁵¹ In short, Ti₃AlC₂ (the synthesis details of Ti₃AlC₂ can be found elsewhere)²⁶⁶ was etched using a solution of LiCl dissolved in 10 wt% HF (1 g Ti₃AlC₂:10 mL of etching solution and Ti₃AlC₂:LiCl ~ 1:5 molar ratio) at room temperature for 24 hours. After etching the mixture was centrifuged, the top liquids were decanted, and fresh de-ionized water was added to the settled powder. The steps of adding fresh DI water, centrifugation, decanting the liquids were repeated multiple times until pH of the decanted liquid was > 5. Afterward, the settled powders were rinsed with 37% HCl (30 mL 37% HCl: 1 g of powder) then centrifuged and the liquids were decanted followed by adding fresh HCl. These HCl washing steps were repeated 4 times. After the HCl washing steps, fresh DI water was used to remove any traces of HCl. While the powders were still wet, they were divided into three portions. One of the portions was vacuum filtered to dry at room temperature. For the other two, one of them was soaked in 1.0 M KCl in DI water and the other in 0.5 M MgCl₂ in DI water, both for 1 hour (40 mL of solution: 1 g of powder). Afterward the mixtures were centrifuged and the liquids were decanted, then the settled powders were soaked for 24 hours in fresh solutions of their corresponding salts (1.0 M KCl for one sample and 0.5 M MgCl₂ for the other). Then the mixture was centrifuged and the liquids were

decanted and fresh DI water was added to remove any excess salts, followed by centrifugation and decanting of liquids. The water-washing step was repeated twice. The washed powders were filtered using a vacuum-assisted filtration setup and allowed to dry freely in air. All the treatments described above were conducted at room temperature.

Solutions of K- and Mg-intercalated MXenes (~34% MXene by wt.) were sonicated in DI water for 1 hour. Using a precision pipette, 1 μL of each MXene solution was drop-cast on a pre-cleaned 5 MHz AT-cut gold-coated quartz crystal microbalance (QCM) and a SiO_2 substrate with pre-patterned interdigitated gold electrodes spaced 2 μm apart. The MXene solutions cast on QCM and SiO_2 substrates formed films composed of networks of H_2O -intercalated flakes. Prior to H_2O vapor sorption measurements, films were placed under 10^{-3} Torr (1.33×10^{-3} mbar) vacuum for 12 hours. The QCM crystals were driven by open-source Pierce oscillator circuits (OpenQCM).³⁷ Frequency shift was measured by Arduino micro microcontroller boards. Frequency shift of the QCM crystals was converted to mass change using the well-known Sauerbrey equation.³⁶ To increase resolution of the QCM signal, a 10 second gate time was implemented. Increasing the gate time enables sub-0.1 Hz frequency resolution during vacuum-based QCM measurements. The 10 second gate time was sufficient to measure the slow kinetics of water sorption/desorption on MXenes. Electrical resistance was recorded using a Keithley 2420 source-meter. Water vapor pressure inside the vacuum chamber was regulated with a mass flow controller. A LabVIEW program was used to record data and control the QCM, Keithley 2420, and mass flow controller. During the experiment, samples were exposed to 90-minute long pulses of H_2O vapor corresponding to $P/P_0 = 0.05, 0.2, 0.4,$ and 0.8 , where P/P_0 is the ratio of H_2O vapor pressure to H_2O vapor saturation pressure at 27°C , so that P/P_0 corresponds to RH. All measurements were performed at $27 \pm 0.5^\circ\text{C}$ inside a modified controlled environmental chamber from Surface Measurement Systems Ltd. Thermogravimetric analysis (TGA) was

carried out using a Discovery TGA from TA Instruments. TGA was performed on MXene powders under nitrogen flow after samples were exposed to air. During the experiment, temperature was ramped from room temperature to 400 °C at a rate of 20 °C/min.

Results and discussion

Water mobility in $\text{Ti}_3\text{C}_2\text{-K}$ ($D = 4.2 \times 10^{-12} \text{ m}^2\text{s}^{-1}$) was found to be more suppressed than that of pristine Ti_3C_2 ($D = 6.9 \times 10^{-12} \text{ m}^2\text{s}^{-1}$),³⁸ possibly due to the combined effect of the spatial confinement²⁸⁹ and strong K^+ ion-water hydration complex. We found that water molecules in the inter-layer space of $\text{Ti}_3\text{C}_2\text{-Mg}$ ($D = 11.1 \times 10^{-12} \text{ m}^2\text{s}^{-1}$) are more mobile.³⁸ Considering that Mg^{2+} forms a stronger hydration complex compared to K^+ , which should result in slower dynamics of water for $\text{Ti}_3\text{C}_2\text{-Mg}$, the contradicting results measured here indicate that the *d*-spacing (*d*-spacing of $\text{Ti}_3\text{C}_2\text{-Mg} > \text{Ti}_3\text{C}_2\text{-K}$) has a dominant effect compared to the nature of ion-water hydration complex. Similar observation was reported from quasi-elastic neutron scattering (QENS) studies of hydrated clays system.²⁹⁰⁻²⁹¹ Mobility of H_2O inside the MXenes suggests that the response time of a MXene humidity sensor would be on the order of 100 seconds. Any additional process, such as chelation, or complex migration would increase response time. It is worth noting that all the QENS measurements were conducted on samples after vacuum annealing at 110°C.³⁸ Thus, the water mobility values discussed above can be considered the lower limit as they reflect mobilities of confined water.

Water interaction with K- and Mg-intercalated MXenes may produce electrical and gravimetric responses in MXene films which can be used for water vapor sensing. Figure 37(a) and (b) show electrical resistance (ΔR) and frequency shift (Δf) when K- and Mg-intercalated MXene films on interdigitated electrodes and QCM crystals are exposed to water vapor. While Frequency shift is associated

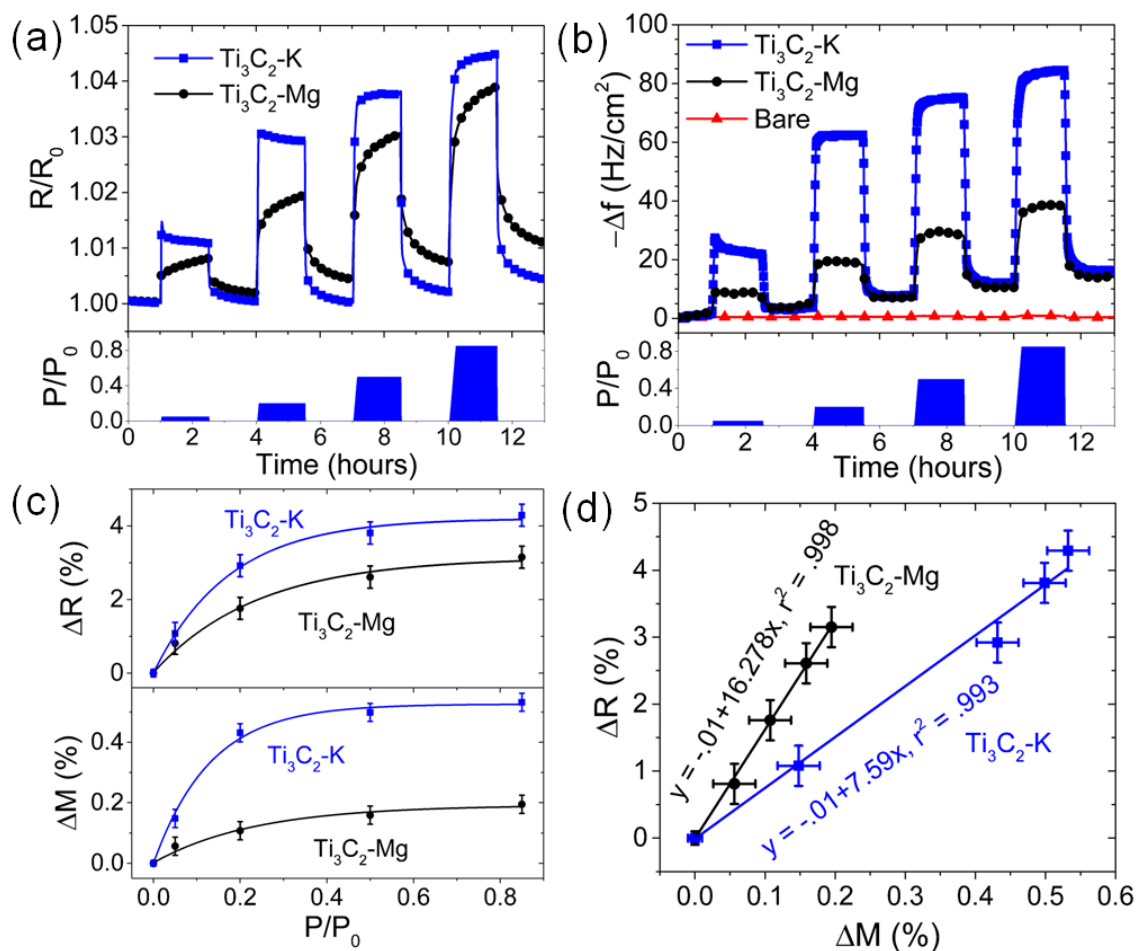


Figure 37. (a) Normalized resistance change (R/R_0) of K- and Mg-intercalated MXenes during exposure to water vapor. H_2O pressure (P/P_0) is shown in lower panel, where P_0 is the H_2O saturation pressure at 27 °C (~23.8 Torr). (b) Normalized frequency shift (Δf) under the same RH conditions. For reference, frequency shift of a bare Au-coated crystal is shown in red. (c) Changes in ΔR and ΔM (film mass) as a function of P/P_0 shown with corresponding exponential fits. (d) Changes in ΔR as a function of ΔM are shown with corresponding linear fits. Figure reproduced with permission.³⁸

with adsorption of water, the changes in ΔR can be attributed to electronic decoupling of individual MXene layers due to inter-layer space increase²⁵¹, charge depletion in the presence of adsorbed H_2O ,^{284, 286} and H_2O -induced chemical modification of the MXene surface.²⁸⁷⁻²⁸⁸ Ti_3C_2 -K exhibits larger changes in resistance and frequency shift than Ti_3C_2 -Mg. The results are consistent with stoichiometric analysis and water-submerged QCM experiments which show that concentration of K^+ ions is roughly twice as high as concentration of Mg^{2+} ions (Table 1), resulting in 50% more water per unit cell in Ti_3C_2 -K than in Ti_3C_2 -Mg (Table S4). This suggests that water capacity of the hydrated MXene network depends on cation concentration rather than d -spacing, and therefore the MXene formula should indicate the number of intercalated ions (Ti_3C_2 - $K_{0.14}$ and Ti_3C_2 - $Mg_{0.07}$). The resistive response of MXenes to water vapor pulses is shown in Figure 5a. Electrical resistance of Ti_3C_2 -Mg film continued to rise during 90 min of water exposure while that of Ti_3C_2 -K film reached stabilization much faster (~ 50 min). Ti_3C_2 -K films also showed higher reversibility, with $>90\%$ of the initial value of resistance and frequency shift being fully recoverable after 90 minutes, compared to 80-85% recovery for Ti_3C_2 -Mg. We speculate that the partial irreversibility is due to trapped water between MXene layers, leading to hysteresis in the hydration/dehydration dynamics of Ti_3C_2 -Mg.

Using the Sauerbrey equation³⁶ and frequency shift of the QCM crystals we estimated that with a 10 second gate time the gravimetric sensor detects 0.025% change in mass of MXene film, corresponding to ~ 35 ng of H_2O per ~ 140 μg of MXene film. The Sauerbrey equation is valid only for acoustically-thin rigid films which are tightly bound to the surface of the quartz oscillator. Changes in viscoelastic properties of the film and slipping at the film/crystal interface complicate the relationship between frequency shift and mass change.²⁹² Shpigel et al showed that viscoelastic contributions to frequency shift are generally non-negligible.²⁶¹ Here, we assumed that frequency shift primarily reflects mass change in the MXene films and we used the Sauerbrey equation to estimate

mass change from Δf . Figure 5c shows a correlation between changes in electrical resistance (ΔR) and film mass (ΔM) after 90 minutes of H₂O vapor exposure at different partial pressures. At $P/P_0 > 0.5$ changes in ΔR and ΔM become small. This likely occurs after all inter-layer spaces are occupied and hydrophilic surface groups are hydrated. Figure 5d shows the relationship between resistance and mass change during H₂O adsorption, which is nearly linear for both Ti₃C₂-K and Ti₃C₂-Mg, suggesting that H₂O sorption is responsible for observed changes. We estimated that MXene-based RH sensors achieve resolution of ~3% RH. The detection limit was estimated to be ~0.2 Torr partial pressure H₂O (corresponding to $P/P_0 = 0.8\%$) for both resistive and gravimetric-based sensing. Sensitivity and detection limits were estimated from Figures 5c and 5d by comparing the response to the background signal. We demonstrated that K- and Mg-intercalated MXene humidity sensors can operate in ~0-85% RH range at room temperature. This is comparable to performance of RH sensors based on metal oxides which show 2% RH sensitivity in 5-99% RH range,²³⁸ graphene oxide sensors which show 4% RH sensitivity in 11- 95% RH range,²⁹³ and conjugated polymers which show 1% RH sensitivity in 33-97% RH range.^{241,}

294

Differences in Ti₃C₂-K and Ti₃C₂-Mg H₂O desorption kinetics are shown in Figure 38. The ΔR and ΔM responses were modeled using an exponential decay with time constant τ . As shown in Figure 6a, H₂O partial pressure does not have a significant effect on τ . The average values of τ for ΔR and ΔM responses to H₂O desorption in Ti₃C₂-K and Ti₃C₂-Mg are shown in Figure 6b. In both materials, the value of τ for the resistive response is larger than τ for the mass change by nearly an order of magnitude, suggesting that H₂O adsorption/desorption is faster than the corresponding electronic changes. Adsorption/desorption of the majority of H₂O occurs on a timescale of 5 minutes or less, while recovery of the electrical resistance occurs on much longer timescale (~30 minutes).

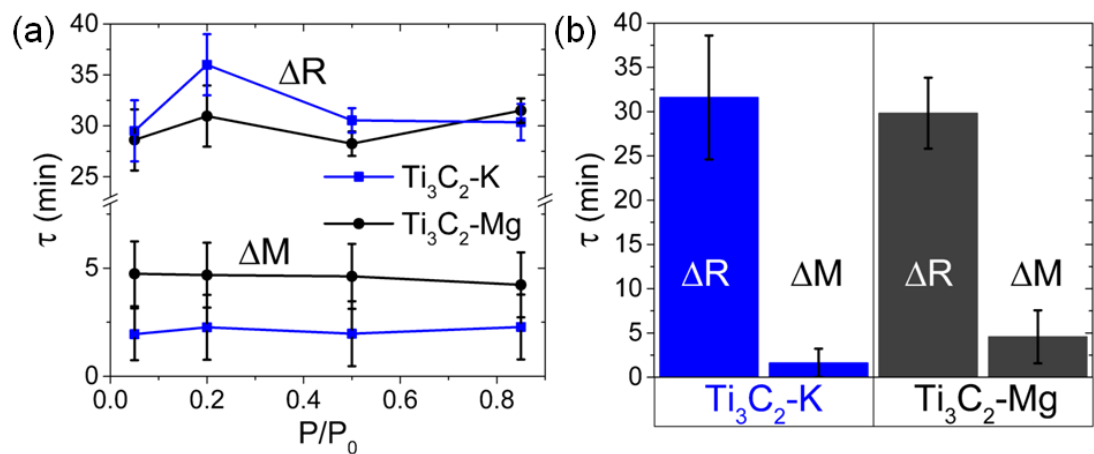


Figure 38. (a) Exponential time constant (τ) for ΔR and ΔM responses during H_2O desorption. Note break in y-axis. (b) Comparison of average value of τ in $\text{Ti}_3\text{C}_2\text{-K}$ and $\text{Ti}_3\text{C}_2\text{-Mg}$. Figure reproduced with permission.³⁸

Finally, we investigated the effect of air and temperature on the ΔR and ΔM responses of $\text{Ti}_3\text{C}_2\text{-K}$ and $\text{Ti}_3\text{C}_2\text{-Mg}$. Figure 39(a) shows the resistance change of MXenes during exposure to 10^{-3} Torr vacuum after films were exposed to ambient air. Over a period of 10 hours in vacuum the resistance of K- and $\text{Ti}_3\text{C}_2\text{-Mg}$ decreases by ~ 14 and 7% , respectively. The change in resistance upon transition of film from air to vacuum is $\sim 5\%$ larger than the response to transition from vacuum to 85% RH. This suggests that air has a large effect on the electrical properties of the MXenes, and the effect is semi-reversible upon exposure to vacuum. Oxidation of MXene flake edges in the presence of air may contribute to the observed irreversibility.²⁹⁵ This suggests that MXenes may undergo charge transfer interaction with components of ambient air. Partial oxidation of MXene flake edges in the presence of air could contribute to the irreversibility.²⁹⁵

QCM proved itself as a very powerful technique to study 2D intercalation electrodes in electrochemical energy storage systems.²⁹⁶⁻²⁹⁷ We studied behavior of MXene films submerged in water using QCM³⁸. Ethanol was chosen as reference liquid since MXene-coated QCM submerged in ethanol showed no detectable change in frequency. The addition of water to ethanol caused a decrease in oscillation frequency (increase in mass) of K- and Mg-intercalated MXene films but not in the pristine MXene, and $\text{Ti}_3\text{C}_2\text{-K}$ adsorbs more H_2O than $\text{Ti}_3\text{C}_2\text{-Mg}$ per unit formula of $\text{Ti}_3\text{C}_2\text{T}_x$. These results agree with results of water vapor adsorption experiments in K- and Mg-intercalated MXene films (Figure 37). The results of thermal gravimetric analysis (Figure 39(b)) suggest that $\text{Ti}_3\text{C}_2\text{-Mg}$ releases less H_2O upon dehydration than $\text{Ti}_3\text{C}_2\text{-K}$, which correlates with the results of water absorption on submerged MXene films. Future studies will focus on effect of cations on dynamics of water-MXene interaction.

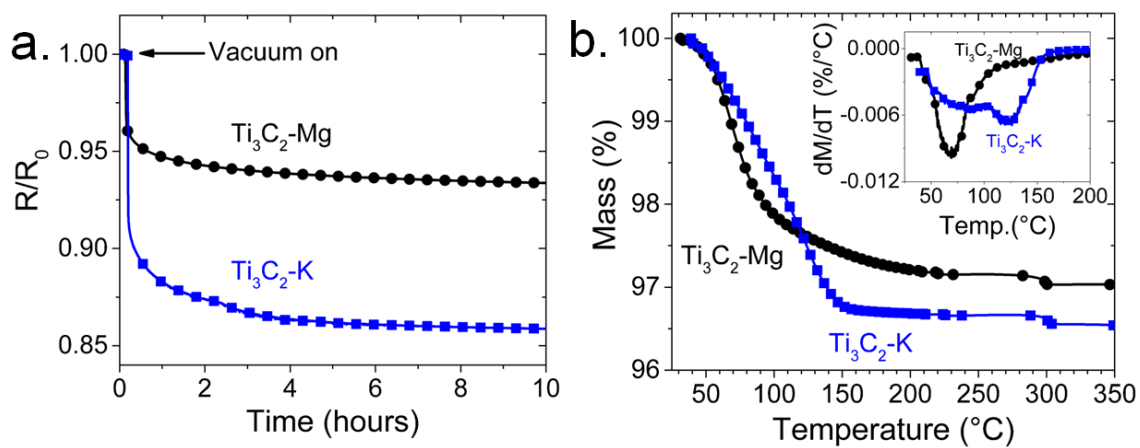


Figure 39. (a) Normalized resistance change upon exposure to 10^{-3} Torr vacuum after MXene films were exposed to air. (b) Normalized mass change of MXenes as a function of temperature. Derivative of mass with respect to temperature is shown in inset. Figure reproduced with permission.³⁸

Conclusions

K- and Mg-intercalated MXenes were investigated as active materials for resistive and gravimetric RH sensing. Neutron scattering combined with *ab initio* calculations³⁸ showed that intercalation of an average 2 water molecules per K⁺ ion and 5 molecules per Mg²⁺ ion led to a pillaring effect which led to an increase in the c-lattice parameters of K- and Mg-intercalated MXenes. By exposing the MXenes to pulses of water vapor and measuring resistance and mass changes in the films, we showed that MXene-based RH sensors had detection limits of ~0.8% RH and can be used in the 0-85% RH range with ~3% resolution. The resistive response to H₂O desorption is slower than mass response by about an order of magnitude due to residual water molecules trapped between MXene layers which have a significant effect on electrical resistance of the MXene network. We observed larger changes in resistance and mass for MXenes exposed to air than MXenes exposed to water vapor, suggesting that interaction of MXene films with components of air has a significant effect on charge transport.

Chapter 10: Mechanisms of environmental response

Chapters 3-9 consisted of studies related to the environmental response of organic small molecules, carbon nanotubes, conjugated polymers, nanocomposite films and MXenes. This chapter draws correlations between the behavior of different materials and summarizes the common mechanisms of environmental response described in previous chapters.

Electrical response to adsorption of gas/vapor arises from a broad range of electronic, ionic and physical mechanisms, including charge transfer between adsorbent and adsorbates, formation of electrical double layers by accumulation of adsorbates at interfaces, and physical swelling of adsorbent materials which decreases the hopping mobility of charge carriers. In water soluble adsorbents, electrical response to water arises from a combination of effects from physical film swelling which increases the distance between electrically conductive domains, an increase in the average dielectric constant due to uptake of water, increased mobility of ions from dissociated salts, and formation of electrical double layers by mobile hydronium ions and protons.

In general, material responses to environment that were observed in the previously-described studies can be associated with three primary mechanisms: (i) sorption- and light-induced charge transfer, (ii) mechano-structural changes induced by sorption of gas/vapor molecules, and (iii) water accumulation at interfaces. Specific examples of each response mechanism are described in the following sections.

Charge transfer

Charge transfer with adsorbates

In organic materials such as metal phthalocyanines and carbon nanotubes, electrical response to environment is primarily governed by charge transfer between adsorbates and the adsorbent material. In metal phthalocyanines oxygen coordinates with the central metal atom⁸⁶ while water interacts at crystallite domain boundaries by hydrogen-bonding⁸⁷⁻⁸⁸. Charge transfer from CuPc to electron-accepting O₂ and H₂O increases hole density in the phthalocyanine domains, leading to higher electrical conductivity and more negative surface potential⁸³⁻⁸⁵. The change in surface potential of CuPc during adsorption of O₂ and H₂O results in modulation of the excitonic transition and bandgap energies. These changes are observable in the Q_A, Q_B and Q_{CT} sub-bands¹²² of the electronic absorption spectrum of CuPc which arises from $\pi \rightarrow \pi^*$ transitions¹¹⁹⁻¹²⁰.

In carbon nanotubes, effects of O₂ and H₂O on CNT networks depend on the abundance of mobile free charge carriers¹⁴⁷. Metallic CNTs transfer charge to O₂ and H₂O, which decreases electron concentration in the film and results in higher electrical resistance. The opposite effect occurs in semiconducting CNT networks due to their p-type behavior. Charge transfer between CNTs and O₂/H₂O alters the bandgap, work function, local density of states, and energy of the semiconductor-metal transition¹⁴⁸⁻¹⁵⁰. The curvature of carbon nanotubes introduces sp³ character to the dominant sp² planar C=C bonding¹⁴⁶, making CNT networks susceptible to partial oxidation which causes locally electron-rich and electron-deficient regions/defects, facilitating the formation of COOH, OH, and CO functional groups^{149, 155}. Adsorption of oxygen leads to hybridization between the valence bands of CNTs and O₂ adsorbates, which increases the

density of states at the Fermi level¹⁵² and results in hole doping behavior¹⁵⁴. Oxygen molecules physisorb with binding energy of ~ 0.25 eV on SWNTs, withdrawing about $e/10$ charge per each adsorbed molecule¹⁵³.

Charge transfer induced by UV irradiation

UV irradiation of adsorbent films can lead to the creation of structural defects, electronic photoexcitation, photodesorption of surface adsorbates, and photoinduced plasmons. Gas/vapor adsorption in the presence of UV irradiation is further complicated by the creation of photoexcited adsorbate molecules which may exhibit strong affinity to the adsorbent or other adsorbate molecules.

Desorption of O₂ CNTs under UV irradiation is primarily mediated by photo-generated π -electron surface plasmons¹⁵⁵. Photon absorption in CNTs may promote Fermi level electrons by as much as 3.5 eV, leading to production of electron-hole pairs and plasmons. Plasmon lifetime is on the order of 1 fs, after which plasmons decay into single-particle hot electron and hole excitations¹⁶³, which can overcome the activation energy barrier of O₂ desorption^{156, 158}. UV irradiation also enhances dissociative chemisorption of O₂ and H₂O on carbon surfaces. Singlet oxygen can be formed by UV photoexcitation of gas-phase triplet O₂ or by interactions between physisorbed triplet O₂ and UV photoexcited carbon allotropes¹⁵⁵. Exposure to singlet O₂ generally leads to the oxidation of CNT networks^{160, 164}. During dissociative chemisorption of oxygen, each O atom rests above a C=C bond bridge site to form a C-O-C complex which destroys the perfect π -bonding between carbon atoms. This may enhance further photooxidation at other C-C bridge sites¹⁵³⁻¹⁵⁴ due to disruption of π -bonding or lead to chemical stabilization of the nanostructure by trapping local photoinduced charge carriers^{155, 160}.

In p-type CNTs, UV absorption enhances downward band bending since the surface photovoltage transports negative charge to the film surface¹⁷⁰. The SPV effect narrows the effective width of the adsorption energy barrier, which increases the probability of charge transport back and forth across the barrier. Excitation in adsorbed O₂ molecules by singlet quenching of the CNT surface or by direct absorption of UV photons¹⁵⁵ increases the probability of electron transfer from adsorbed O₂ back to the CNT, facilitating molecular desorption. Since UV irradiation effectively lowers energy barriers for both adsorption and desorption, both sorption rates may be enhanced in the presence of UV light. During exposure to O₂ and H₂O, UV irradiation of CNTs increased the electrical response and decreased the detection limits of s-SWNT, m-SWNT, and MWNT networks by roughly an order of magnitude⁵⁹.

Dissociative chemisorption of H₂O from CNTs becomes favored over O₂ when oxygen or hydrogen defects are present on the CNT surface. UV-enhanced removal or addition of C-H and C-OH groups formed by H₂O dissociation allows for control of reversible hydrophobic-hydrophilic transitions on the surface¹⁵³, where the OH moiety acts as an electron acceptor, behaving similarly to physisorbed O₂¹⁴⁹.

In ZnO/SU-8 hybrid nanocomposite films, gravimetric response to oxygen and water vapor increased by 50–500% when adsorption took place under UV irradiation. The effect of UV irradiation was attributed to photo-induced decomposition of the photo-acid generator triarylsulfonium hexafluoroantimonate ((Ar)₃S⁺SbF₆⁻), which acts as a catalyst for cationic polymerization by opening SU-8 epoxy rings during thermal annealing, to H⁺SbF₆⁻, resulting in a chemically-stable cross-linked SU-8 matrix²¹⁷⁻²¹⁹. H⁺SbF₆⁻ is strongly hydrophilic and forms fluoroantimonic acid hexahydrate (H⁺SbF₆⁻ + 6H₂O) upon exposure to water²²⁰. In this case, UV irradiation of the ZnO/SU-8 composite resulted in fully reversible

surface hydrophilicity and increased surface potential and adsorption energies for oxygen and water molecules ²²⁶.

Mechano-structural changes

Adsorption of gas/vapor molecules can lead to significant changes in mechanical, structural and morphological properties of adsorbent films due to disruption of bonds in the adsorbent, swelling of the adsorbent, increased mobility of ions in the adsorbent, and decoupling of the adsorbent from the substrate. Structural and morphological response to adsorption is strongly correlated to electrical and viscoelastic properties of the adsorbent, as charge carrier mobility and elastic modulus are often governed by the underlying morphological structure.

In CuPc films, O₂ and H₂O adsorption may facilitate fracture, displacement, and rearrangement of CuPc domains due to disruption of intermolecular and molecule-substrate bonding⁹¹. We observed evidence of mechano-structural change in CuPc likely due to slipping motion between CuPc crystallites and between CuPc and the Au electrode of the QCM oscillator which was caused by preferential adsorption of H₂O/O₂ molecules on gold. A similar effect was observed in semiconducting SWNT networks. We proposed that the effect is reversible and stems from perturbation of van der Waals interaction between CNTs and preferential adsorption of electron acceptors on gold, which leads to partial delamination of s-SWNTs from the QCM surface⁵⁹.

Film swelling and formation of electrical double layers were observed in PEDOT:PSS and CuPcTs films using ellipsometry and spectroscopic impedance⁵⁶. In water-soluble CuPc films, ionic dissociation and H₂O multi-layer formation at RH > 70% can result in creation of a mechanically-unstable MPC-H₂O pseudo-solution mixed phase¹¹⁶⁻¹¹⁷ which allows CuPcSO₃ migration along

the substrate surface due to interaction with H₂O layers. Mobility of CuPc(SO₃⁻)₄ ions results in morphological changes including domain displacement and fracture^{91, 112}. Similar effects were observed in PEDOT:PSS, in which hydrogen bonding between water molecules strains existing hydrogen bonds in the PSS matrix and leads to inter-domain decoupling and decohesion of the PEDOT:PSS complex, decreasing rigidity of the polymer matrix and resulting in significant swelling of the film¹⁹⁴. As estimated using spectroscopic ellipsometry, optical film thickness swelled to 150% of its original thickness as RH increased from 1% to 85%⁵⁶. The degree of film swelling is dependent on the ratio of hydrophilic to hydrophobic moieties in the film, the aspect ratio of domains, and mobile ion concentration.

In MXenes, it was shown previously that adsorption of water can lead to stiffening of Ti₃C₂ film due to formation of highly ordered water layers between Ti₃C₂ sheets²⁵⁹. Ghidui et al. showed that K⁺, Na⁺, Li⁺, Ca²⁺-intercalated Ti₃C₂ undergoes an increase in basal spacing during water intercalation between 2D Ti₃C₂ sheets. We used neutron scattering coupled to molecular dynamics and *ab initio* calculations to show that intercalation of an average 2 water molecules per K⁺ ion and 5 molecules per Mg²⁺ ion led to a pillaring effect which caused an increase in the c-lattice parameters of K- and Mg-intercalated MXenes. We also showed that MXene films undergo viscoelastic change when their water content increases, which may arise due to slipping between MXene sheets or the contribution of loosely-held water at hydrophilic -OH, -O, and -F terminations in Ti₃C₂³⁸. Our results indicate that both soft films such as polymers and organic small molecules and rigid films such as MXenes may exhibit viscoelastic response to adsorption of water.

Water layer formation

Water accumulation at interfaces

Many hydrophilic materials show evidence of multilayer water formation on domain surfaces under high humidity conditions ($RH > 70\%$). Material response to environment often exhibits strong nonlinearities when a multi-layer water meniscus has formed on the film surface due to electrical and chemical interactions at the solid-liquid interface, resulting in changes to electrical, optical, dielectric, and mechano-structural properties of the underlying adsorbent material.

In water-soluble CuPc, multilayer water formation on domain surfaces may result in switching from dominant electronic to ionic conduction, which increases film conductivity⁸⁹⁻⁹⁰. CuPcTs undergoes adsorption of water at hydrophilic sulfonyl/salt groups, which leads to dissociation of Na^+ ions from $Na_4CuPc(SO_3)_4$. At $RH > 60\%$, surface water clusters begin to merge, which allows ion diffusion throughout the water-percolation network, resulting in dielectric screening of CuPcTs domains by H_2O and mobile ions at high frequencies. Multilayer water formation at high RH conditions can result in creation of a mechanically-unstable MPc- H_2O pseudo-solution mixed phase¹¹⁶⁻¹¹⁷ which enables $CuPcSO_3$ migration along the substrate surface due to interaction with H_2O layers. Mobility of $CuPc(SO_3^-)_4$ ions can result in significant morphological changes including domain displacement and fracture^{55, 91, 112}. Similar response is observed in PEDOT:PSS, where strong van der Waals and hydrogen bonding between water molecules becomes a dominant force after H_2O monolayer formation. Exposure to $RH > 80\%$ leads to H_2O multilayer formation and condensation on the PEDOT:PSS surface^{175, 179}, which increases the mobility of ions, facilitates

significant film swelling, and leads to dielectric screening of the film by the water and mobile ions⁵⁶.]

In MXene films, electrical properties are governed by the high conductivity of 2D MXene sheets. Impedance spectroscopy performed on Ti_3C_2 suggests that the majority of resistance and capacitance in MXene films arises from electron hopping across grain boundaries while bulk Ti_3C_2 grains contribute insignificantly to the film impedance^{267, 269}. Water accumulation near grain boundaries is therefore the likely dominant mechanism underlying Ti_3C_2 electrical response to water. Evidence of voltage drop due to accumulation of adsorbed water at gold- Ti_3C_2 junctions was also observed²⁶⁸. Changes in electrical resistance of ion-intercalated Ti_3C_2 were attributed to electronic decoupling of individual MXene layers due to inter-layer space increase²⁵¹, charge depletion in the presence of adsorbed H_2O ,^{284, 286} and H_2O -induced chemical modification of the MXene surface.²⁸⁷⁻²⁸⁸

Effects of water on ion mobility

The mobility of ions governs conductivity and dielectric properties in many adsorbent materials. Adsorption of water can lead to dissociation of salts into mobile ions which can migrate through layers of adsorbed water to form electrical double layers at domain interfaces. In CuPcTs, the presence of H_2O at SO_3Na groups induces salt dissociation into Na^+ and $\text{CuPc}(\text{SO}_3^-)_4$ ions¹¹⁵⁻¹¹⁶ which contribute to charge transport at $\text{RH} > 45\%$ ¹¹³. Under high humidity conditions ($\text{RH} > 70\%$), salt dissociation and H_2O multi-layer formation can result in creation of a mechanically-unstable $\text{MPc-H}_2\text{O}$ phase¹¹⁶⁻¹¹⁷ in which CuPcSO_3 migration may result in significant morphological changes including domain displacement and fracture^{91, 112}. The presence of Na^+ ions in percolated H_2O networks leads to

subsequent changes in optical properties and dielectric screening of CuPcTs domains at high frequencies.

In PEDOT:PSS, the hydrophilic PSS electrolyte contains anionic immobile sulfonic acid groups and protons (hydronium ions) as counter ions. At RH > 30%, water loading of PSS chains permits hopping of the protons between sulfonic acid groups¹⁸³, leading to increased ionic mobility and the formation of electrical double layers. This effect increases capacitance of the film due to the increase in average dielectric constant.

Systems with mixed adsorption kinetics

Film response to gas/vapor adsorption often occurs as a result of multiple processes which consist of both fast and slow kinetics. In some cases, convolution of several response mechanisms makes it difficult to differentiate between distinct processes. In other materials, the observation of mixed kinetics provides important clues for unfolding the effects on environment on material properties.

In many adsorbents, including CuPc, high porosity enables fast response due to the high surface area available for interaction with adsorbate molecules^{87, 97}. Since response time is often limited by slow diffusion of adsorbates into the film bulk⁸³ it is inversely proportional to film thickness⁸². As thickness decreases, charge transport layers lie closer to the film/gas interface and the effects of adsorption-induced surface trap states are enhanced⁹². While mass loading during adsorption of gas/vapor on CuPc occurred over ~10 minutes, electrical resistance changes occurred over ~1 hour, suggesting that the resistive CuPc gas/vapor response is dominated by slow diffusion of adsorbates into the film bulk, while mass change occurs by rapid adsorption at active surface sites⁵⁷.

The H₂O-CuPcTs interaction showed evidence of multiple processes with distinct kinetics. To model the kinetics, we used a two-step pseudo-first order kinetic process. The first step was associated with adsorption of H₂O on hydrophilic sulfonyl sites at the periphery of CuPcTs grains, which did not lead to significant changes in optoelectronic properties of the film. The second process, which became active at RH > 60%, was related to H₂O saturation of CuPcTs surface sites and diffusion of water into bulk CuPcTs grains⁵⁵.

PEDOT:PSS exhibited similar evidence of multi-process environmental response. We observed that mass loading, DC electrical conductivity, optical conductivity, and optical bandgap changes in the film occurred in three primary RH regimes. Significant film response was observed at low (RH < 10-25%) and high (RH > 60-75%) humidity conditions while insignificant changes occurred at mid-RH conditions (25% < RH < 60%). It was speculated that the three regimes correspond to three distinct physical processes: rapid H₂O adsorption at active PSS sites at low RH, slow H₂O adsorption and diffusion throughout the bulk film at mid-RH, and H₂O saturation and multilayer water formation on the film surface at high RH⁵⁶.

MXenes showed evidence of multiple response kinetics as well. We found that the gravimetric response of ion-intercalated MXenes to water was 10 times faster than the electrical response, which suggests that H₂O-induced swelling/contraction of channels between MXene sheets resulted in trapping of H₂O molecules that acted as charge-depleting dopants³⁸. Since the primary electrical conduction channels are often located in the bulk film near bottom electrodes, it is common that gravimetric response of films occurs quickly (seconds to minutes) as adsorbates interact with active sites on the film surface, and electrical response occurs slowly (minutes to hours) as trapping, un-trapping,

and diffusion of adsorbates inside the bulk film gradually alters film conductivity near the electrodes.

Chapter 11: Future opportunities

There are many opportunities for future development of the materials characterization workflow described in this study. This chapter describes four potential pathways for future growth of the system which will benefit materials efforts in the greater research community. Since the system described in this study is located inside CNMS at ORNL, descriptions of future opportunities are tailored toward ongoing efforts at CNMS and ORNL. However, the same methodologies may be applied at other research institutions or industrial facilities.

Development of material expert system

Development of expert systems in which task-specific expertise is transferred from human researchers to computer models has been one of the longest-running and most successful applications of advanced statistics and machine learning²⁹⁸⁻²⁹⁹. Interest in expert systems for design, selection, and prediction of material properties has grown steadily^{71, 300}, fueled in part by availability of high performance computing resources and comprehensive materials databases¹¹⁻¹⁴ such as those assembled by the Materials Genome Initiative¹⁵. A materials expert system may be comprised of databases, models and algorithms which are built from results of experiments and simulations^{71, 299}. The primary strength of expert systems is that performance improves with training, much like a human researcher³⁰⁰. Since the expert system can only make predictions based on data included in the model, increasing the quantity and quality of input data is vital for improving performance^{8, 301}.

High-performing materials expert systems require input data across a broad range of material properties. The availability of high-performance computing resources, expertise in theory and modeling, and automated materials characterization capabilities at CNMS provide the opportunity for development of a novel materials expert system which directly interfaces with experiment and

simulation software. Other organization with access to large amounts of tabulated materials data, such as National Institute of Standards and Technology (NIST)³⁰² and companies such as Citrination³⁰³ are also well-suited for development of cutting-edge materials expert systems.

In contrast to traditional database systems which rely on manual input of data from experienced researchers, the proposed system will enable automated transmission of experimental data directly into a materials database along with metadata descriptors such as sample synthesis information, sample age and history, measurement parameters and settings, and environmental conditions present during each measurement. The database will be coupled to machine learning and statistical models to form an expert system for predicting material properties and forecasting sample response to dynamic environmental conditions. The expert system will learn from data acquired during each experiment, including those experiments which are not analyzed or utilized by human researchers, and will be coupled to materials theory and modeling efforts in order to integrate experimental and computational approaches. Growth of the expert system will support a broad range of research and computing missions at ORNL, including soft material research efforts.

Combinatorial synthesis robot

To accelerate the rate of materials discovery and deployment, researchers are becoming increasingly reliant on combinatorial approaches for synthesis and screening of novel materials³⁰⁴. Approaches for high-throughput synthesis of materials for catalysis³⁰⁵, electronics³⁰⁶, polymers³⁰⁷ and bio-interfacing³⁰⁸ have garnered significant interest. However, the full benefits of rapid synthesis are not realized unless synthesized materials are screened for functional properties. Tabulated material properties can then be used to optimize the conditions of

subsequent synthesis cycles³⁰⁴. For implementation of this closed-loop feedback strategy, combinatorial synthesis is increasingly being coupled to characterization workflows in which rapid mapping of functional properties across compositional phase diagrams is performed³⁰⁷.

The workflow elucidated in previous chapters provides a useful platform for high-throughput multi-functional materials characterization which can provide rapid feedback to a materials synthesis robot, closing the loop between automated synthesis, characterization, and optimization of functional properties. A future opportunity for project development involves coupling the characterization system to a synthesis robot which deposits thin films under variable conditions (i.e. varying chemical composition, deposition temperature, spin coating speed) for sensing applications. The IMES system can be used to characterize electrical and gravimetric/viscoelastic response of the deposited films to changing environmental conditions, providing insight into the effects of synthesis conditions on environmental response. Results can be used as inputs for optimizing the next round of film depositions for improving sensing performance (i.e. response time, reversibility, sensitivity) for example.

CNMS at ORNL is uniquely positioned for integration of synthesis and characterization workflows because of the well-developed in-house synthesis programs and access to characterization instrumentation and expertise. The proposed synthesis robot may be particularly relevant to quantum information science (QIS) efforts at ORNL, which aim to apply quantum principles and techniques to applications in sensing, computing and communication. Modularity and flexibility of software and sample environments associated with IMES enables the possibility of integrating multi-functional characterization tools with a broad range of synthesis systems for full automation of the synthesis-characterization feedback loop.

Other organizations which have employed successful combinatorial synthesis programs, such as the Air Force Research Laboratory³⁰⁹, and the Japanese National Institute of Advanced Industrial Science and Technology (AIST)³¹⁰, are well-suited to develop multifunctional characterization tools for coupling with established combinatorial synthesis systems.

Simulations with real-time input

Computer simulation has joined experiment and theory to become a principal tool in materials research. Simulations typically utilize well-established modeling techniques such as density functional theory (DFT), molecular dynamics (MD) or finite element modeling (FEM) to augment results of laboratory experiments for establishing a coherent picture of material behavior. Simulations are often performed after experiments have been completed so that experimental response can be used as a framework for assessing relevance of the simulation results. However, sequential implementation of experiments and simulations is time-consuming and requires experienced researchers to acquire experimental data and configure the simulation model. Simulations can be performed more efficiently if they are run concurrently with experiments. Further efficiencies may be realized if simulations are configured to accept real-time experimental results as inputs rather than manual input from researchers.

Traditionally, on-line simulations were not feasible due to limited availability of computational resources, but interest in real-time simulation of material behavior is growing³¹¹⁻³¹². Algorithmic developments and increases in computational power have enabled an explosion of materials-modeling workflows which leverage experimental data and machine learning inputs to augment well-developed materials simulation techniques^{8, 301}.

CNMS is well-positioned to leverage the high-performance computing resources at ORNL with expertise in theory and modeling to enable direct coupling of simulations to experiments. For example, results from multi-functional materials characterization may be used as inputs for established molecular dynamics code which simulates results of the experiment in real-time. Coupling of experiment to modeling can result in an iterative simulation tool in which modeling parameters are based on real-time experimental results. The proposed system will allow real-time updating of model parameters as additional experimental data is acquired, without the need for human intervention. An opportunity for future development of the characterization system described in this work involves integration of materials modeling software into the experimental control software. This enables direct, rapid interfacing between experimental results and simulation software, allowing adaptive on-the-fly modeling as new experimental results are acquired. The proposed system links multi-functional characterization to high-performance computational modeling, resulting in a new integrated platform for the study of a broad range of materials.

In situ diagnostics on X-ray and neutron beamlines

Structure and morphology play primary roles in governing conductivity, tribology, mechanical longevity/stability and interfacial behavior of materials³¹³⁻³¹⁵.

Understanding the effect of material structure on functional properties is critical for knowledge-based development of new materials and tuning of behavior toward specific end-use applications³¹⁶, including development of high-interest materials such as conductive, adsorbent, self-healing³¹⁷, and bio-interfacing materials³¹⁸⁻³²⁰. Structural response of materials is particularly important in the case of sorbents and electrodes which may undergo structural/morphological changes during interaction with solvents or analytes^{38, 251, 321-322}.

Mapping of structure-property relationships across compositional phase diagrams has become a principal mode of high-throughput material characterization, enabled by improvements in combinatorial materials synthesis techniques³⁰⁷. The characterization methods described in this work enable multi-functional probing of material properties under controlled environment but linking functional properties to structural/morphological response remains challenging. In contrast, X-ray and neutron beamlines used for structural/morphological characterization of thin films often lack electrical/optical/gravimetric channels for functional probing, which prevents real-time observation of the structure-functional relationship under dynamic environments. Real-time simultaneous monitoring of structural and functional properties is needed for observation of metastable mechano-electrical and chemical transformations.

Small-angle and grazing-incidence scattering experiments impose constraints on sample size and uniformity, as the size of the beam footprint is often on the order of centimeters. This requires that thin film samples deposited from solution be cast uniformly on substrates over large area by spin-coating for example, which imposes limits on which materials may be suitable for such measurements. In addition, the time scales associated with in situ beamline experiments must be considered, since neutron-based measurements may require on the order of ~10's of minutes between each sample acquisition. This limits the range of kinetics which can be observed when samples are exposed to dynamic environmental conditions. However, the response of many adsorbent films occurs slowly enough that neutron-based techniques may still enable observation of interaction kinetics.

CNMS is uniquely positioned to combine functional and structural/morphological characterization platforms because of its proximity and access to the Spallation Neutron Source (SNS) at ORNL. SNS capabilities include small-angle X-ray scattering (SAXS), grazing incidence X-ray diffraction (GIXRD) and X-ray

reflectivity (XRR) which allow probing of phase composition, domain size, thickness, and density of thin films. Neutron beamlines such as the liquids reflectometer beamline (BL-4B) at SNS enable probing of soft thick films, bulk materials and evolution of film structure at solid-liquid interfaces. Neutrons are particularly well-suited to detect low-atomic number elements with high neutron cross sections such as hydrogen, carbon and oxygen, enabling study of sorption dynamics of commonly-studied analytes such as H₂O and CO₂ across a broad range of materials and interfaces^{38, 323-324}. Other world-class neutron sources which may greatly benefit from the incorporation of multimodal in situ diagnostics include the China Spallation Neutron Source³²⁵, ISIS Spallation Neutron Source³²⁶, and the Los Alamos Neutron Science Center³²⁷.

A potential high-impact future research project involves development of a controlled sample environment on X-ray or neutron beamlines which enables in situ functional diagnostics of materials on the beamline. Development of the system will allow simultaneous structural/morphological and functional characterization of thin films under controlled environments, providing insight into the structure-function relationship under dynamic ambient conditions. This capability will support a broad range ORNL materials science efforts, including studies of electrode materials which undergo structural transformation during ion sorption/intercalation, polymer films which experience swelling during sorption of adsorbates and solvent molecules, and flexible electronic materials exhibiting strain during exposure to repeated bending cycles. The multi-functional diagnostics system on neutron and X-ray beamlines will provide a powerful tool for elucidating the structure-function relationship under complex environments.

Chapter 12: Conclusions

Improvements in high-performance computing, data analytics, and robotics offer transformational opportunities for the rapid design, modeling and development of novel functional materials. Before their deployment, new materials must be screened for stability and behavior under a broad range of ambient environmental conditions. Due to constraints related to instrumentation, experimental design, and data processing, multifunctional materials characterization is often time-consuming and requires input from experienced human researchers. We developed an integrated system and associated workflow to enable multi-sample multi-functional characterization of materials under controlled environments. Custom software which controls the system allows automated selection of experimental settings, data acquisition, and real-time data processing and analytics. Results from data analysis are used as feedback into the control software, enabling real-time adjustment of experimental conditions, which minimizes the need for an experienced human operator. The system and associated software have been used to probe the environmental stability and sensing performance of a broad range of functional materials including polymers, organic small molecules, biomolecules, perovskites, nanotubes, graphene, MXenes, ionic liquids, metal oxides and hybrid nanocomposites. We found that material response to environment was generally mediated by charge transfer with adsorbate molecules, mechano-structural changes caused by diffusion of adsorbates into adsorbent films, production of mobile ions due to salt dissociation and formation of surface water layers, and photoexcitation of adsorbents by UV radiation. Material response often exhibited mixed-kinetics consisting of rapid gravimetric response during sorption of adsorbates on active surface sites, and slow electrical response resulting from diffusion of adsorbates into the bulk films.

Future opportunities for development of the system and workflow include (i) integration of a combinatorial synthesis robot with multi-functional materials characterization platform to close the feedback loop between synthesis and

function, (ii) integration with computational modeling for real-time feedback between experiment and simulation, (iii) interfacing the characterization system with database infrastructure for creation of a materials expert system, and (iv) integrating of functional characterization platform with X-ray and/or neutron beamlines for in situ probing of structure-function relationships under controlled environment. The ideal system will integrate elements of each of the proposed future development opportunities, resulting in an advanced tool which utilizes a combination of automated materials synthesis, multimodal structure-function characterization and modeling, and creation of a comprehensive materials expert system.

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